

# Crystals and Vibes

Tyler C. Sterling

*Department of Physics, University of Colorado Boulder, Boulder CO,  
80309, USA*

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*The miracle is not that electrons behave oddly... the miracle is that when you take  $10^{27}$  electrons, they behave like cheese.*

— Allan Adams

## Abstract

This document is supposed to be a “guide” to what I do. It’s not coherent story yet... but is rather a constantly evolving “work-in-progress.” In it’s current form, this is a loose set of notes that serves two main purposes: (i) this is where I consolidate references for things I intend to learn in the future, but don’t have time or energy to attack right now. (ii) This is where I detail derivations and notes on topics I am learning or have learned so that I can refer to them later. The eventual goal is to have a “hand-book” for my research (both for my own reference and anyone interested in doing similar stuff). This is also an attempt to satisfy a request from my PhD advisor: circa Spring 2021, Dmitry asked me to give a talk to him and my lab mates explaining how my research works so they could be up-to-date on the field. Better late than never ...

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## 1 Introduction

These are my notes on modelling the dynamics of atoms in solids. I mainly intend to focus on ordered crystals, so the dynamics is formulated in terms of phonons, the “quasiparticle”<sup>1</sup> associated with displacements of the atoms from their perfectly ordered equilibrium positions. I’ve also look at disordered solids and molecular crystals... if I end up needing to generalize for these cases, I’ll add more here. Right now, I’m interested in wacky crystals with strong electron-phonon coupling, so this document necessarily includes lots of electronic structure theory.

This document will, at least in the first-pass, mainly focus on deriving results that are accessible to density functional theory. We will look at how calculations are done in practice, usually with the goal of *quantitative* comparison to experiments. I plan to venture into explicit many-body calculations in the future, so I will add that stuff here too when I am finally not too stupid to know what’s going on.

## 2 Modern Computational Physics

Later on, we will mainly be talking about solids. Usually, we will further specialize to ordered crystals. Many of the tools we will use are familiar in the field of solid state physics (e.g. Bloch’s theorem, Brillouin zones, Fourier series and transforms). However, we need to lay down some formal theory first before specializing to crystals. Let’s do that now. The following discussion will be general; it is applicable to gases, liquids, ordered and disordered solids, and even plasmas<sup>2</sup>.

### 2.1 The Condensed Matter Hamiltonian

In the absence of an external potential, the most general Hamiltonian to describe condensed matter physics is [29, 75]

$$\hat{H} = \hat{H}_e + \hat{H}_n + \hat{H}_{e-n}. \quad (1)$$

It is the sum of the electronic Hamiltonian,  $\hat{H}_e$ , the nuclear Hamiltonian,  $\hat{H}_n$ , and the Hamiltonian for their interaction,  $\hat{H}_{e-n}$ . This is basically the *theory of everything* in

<sup>1</sup> more precisely, a “collective mode”

<sup>2</sup> Though one of the approximations, i.e. Born-Oppenheimer approximation, probably isn’t applicable in plasma physics.

condensed matter physics. Anything interesting that we can observe in materials science is buried in this equation: magnetism, superconductivity, metal-insulator transitions, etc.

In the position-space representation, the electronic sector is

$$\begin{aligned}\hat{H}_e &= \hat{T}_e + \hat{V}_{e-e} \\ \hat{T}_e &= \sum_i^{N_e} \frac{\hat{p}_i^2}{2m_e} \\ \hat{V}_{e-e} &= \frac{k}{2} \sum_{i \neq j}^{N_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}\end{aligned}$$

$\hat{T}_e$  is the electronic kinetic energy operator with  $\hat{p}_i \equiv -i\hbar\nabla_{\mathbf{r}_i}$  the momentum operator acting on the  $i^{th}$  electron. The kinetic energy sum runs over all electrons.  $\hat{V}_{e-e}$  is the mutual Coulomb interaction between all the electrons, with  $k$  Coulomb's constant.  $m_e$  is the electronic mass and  $e$  is the elementary charge. The denominator is the distance between the electrons, with lower-case  $\mathbf{r}$  denoting electronic coordinates.

Similarly, the nuclear Hamiltonian is

$$\begin{aligned}\hat{H}_n &= \hat{T}_n + \hat{V}_{n-n} \\ \hat{T}_n &= \sum_I^{N_n} \frac{\hat{P}_I^2}{2M_I} \\ \hat{V}_{n-n} &= \frac{k}{2} \sum_{I \neq J}^{N_n} \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}\end{aligned}$$

Here,  $\hat{P}_I \equiv -i\hbar\nabla_{\mathbf{R}_I}$  is the nuclear momentum operator with the kinetic energy sum running over all atoms.  $\hat{V}_{n-n}$  is the nuclear Coulomb interaction.  $M_I$  is the mass of the  $I^{th}$  atom and  $eZ_I$  is its charge. The denominator is the distance between the atoms with upper-case  $\mathbf{R}$  denoting nuclear coordinates.

Finally, we have the interaction between electrons and nuclei:

$$\hat{H}_{e-n} = \hat{V}_{e-n} = -k \sum_i^{N_e} \sum_I^{N_n} \frac{e^2 Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$

Solutions of eq. 1 in coordinate space are the wave-functions  $\Psi(\{\mathbf{r}, \mathbf{R}\})$  which depend explicitly on both the coordinates of the electrons and the nuclei.

$$\hat{H}\Psi(\{\mathbf{r}, \mathbf{R}\}) = \mathcal{E}\Psi(\{\mathbf{r}, \mathbf{R}\}) \quad (2)$$

The notation  $(\{\mathbf{r}, \mathbf{R}\})$  is supposed to imply "... depends explicitly on the combined set of nuclear and electronic coordinates." This is all well-and-good, but it turns out that if the number of the particles is more than a few, eq. 2 is unsolvable on even the best supercomputer. So we will need to make some simplifying assumptions.

### 2.1.1 The Born-Oppenheimer Approximation

The first is the *Born-Oppenheimer* or *adiabatic* approximation [14, 67]. We make the ansatz that  $\Psi(\{\mathbf{r}\}, \{\mathbf{R}\}) = \chi(\{\mathbf{R}\})\Phi(\{\mathbf{r}\}, \{\mathbf{R}\})$ . The new notation  $(\{\mathbf{r}\}, \{\mathbf{R}\})$  means “... depends explicitly on the set of electronic coordinates but only parametrically on the set of nuclear coordinates.” While this type of notation is very explicit, it’s more cumbersome to typeset. Let’s be lazy and instead use  $\Psi(\{\mathbf{r}, \mathbf{R}\}) \equiv \Psi(\mathbf{r}, \mathbf{R})$  and  $\Psi(\{\mathbf{r}\}, \{\mathbf{R}\}) \equiv \Psi(\mathbf{r}; \mathbf{R})$ ; the semi-colon separates the explicit from parameteric dependence on the coordinates.

Define the Born-Oppenheimer Hamiltonian for the electrons

$$\hat{\mathcal{H}}_e = \sum_i^{N_e} \frac{\hat{p}_i^2}{2m_e} + \frac{k}{2} \sum_{i \neq j}^{N_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - k \sum_i^{N_e} \sum_I^{N_n} \frac{e^2 Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad (3)$$

For now, the curly font on  $\hat{\mathcal{H}}$  means it’s a Born-Oppenheimer Hamiltonian. Suppose  $\Phi(\mathbf{r}; \mathbf{R})$  is an eigenstate of  $\hat{\mathcal{H}}_e$  with eigenvalue  $\mathcal{E}_e(\mathbf{R})$ .  $\Phi(\mathbf{r}; \mathbf{R})$  is an approximation to the true many-body wave-function of the electrons. It’s clear that  $\Phi(\mathbf{r}; \mathbf{R})$  and  $\mathcal{E}_e(\mathbf{R})$  depend only parametrically on the positions of the nuclei. It’s common to call the electron-nuclear Coulomb interaction in eq. 3  $V_n(\mathbf{r})$  and simply treat as an external potential in the electronic problem.

We want to insert  $\Psi(\mathbf{r}; \mathbf{R})$  into the full Hamiltonian in eq. 1, but we have to be careful and remember that  $\hat{P}^2 = -\hbar^2 \nabla_{\mathbf{R}}^2$  acts on both  $\chi(\mathbf{R})$  and  $\Phi(\mathbf{r}; \mathbf{R})$ . The result is

$$\begin{aligned} \hat{H}\Psi(\mathbf{r}; \mathbf{R}) &= \Phi(\mathbf{r}; \mathbf{R}) \left[ \sum_I^{N_n} \frac{\hat{P}_I^2}{2M_I} + \frac{k}{2} \sum_{I \neq J}^{N_n} \frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \mathcal{E}_e(\mathbf{R}) \right] \chi(\mathbf{R}) \\ &\quad - \chi(\mathbf{R}) \sum_I^{N_n} \frac{\hbar^2}{2M_I} \nabla_{\mathbf{R}_I}^2 \Phi(\mathbf{r}; \mathbf{R}) - \sum_I^{N_n} \frac{\hbar^2}{M_I} \nabla_{\mathbf{R}_I} \Phi(\mathbf{r}; \mathbf{R}) \cdot \nabla_{\mathbf{R}_I} \chi(\mathbf{R}) \\ &= \mathcal{E}'\Psi(\mathbf{r}; \mathbf{R}) \end{aligned} \quad (4)$$

The prime on  $\mathcal{E}'$  is to distinguish from the exact many-body eigenvalue  $\mathcal{E}$  in eq. 2. The electronic energy,  $\mathcal{E}_e(\mathbf{R})$ , is the eigenvalue of the Born-Oppenheimer Hamiltonian eq. 3, but its effect in eq. 4 is to act as a “potential energy” for the nuclei. The essence of the Born-Oppenheimer approximation is to ignore the second line in eq. 4. For the first term, this is justified since the variation of kinetic-energy with respect to atomic coordinates of the electrons is small. This might be violated at large temperature, but in most condensed matter settings, it’s safe to ignore this term. Ignoring the second term is the same as neglecting electron-phonon coupling (see ref. [71], exercise 4.1). **This is okay sometimes, but electron-phonon coupling can be very important in many cases [?]. This document will probably look heavily at electron-phonon coupling.**

We have split the problem of the full interacting system of electrons and nuclei into the following set of (approximate) equations that describe the dynamics of the set of nuclei and electrons. For the electrons

$$\begin{aligned} \hat{\mathcal{H}}_e \Phi(\mathbf{r}; \mathbf{R}) &= \left[ \sum_i^{N_e} \frac{\hat{p}_i^2}{2m_e} + \frac{k}{2} \sum_{i \neq j}^{N_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + V_n(\mathbf{r}) \right] \Phi(\mathbf{r}; \mathbf{R}) \\ &= \mathcal{E}_e(\mathbf{R}) \Phi(\mathbf{r}; \mathbf{R}) \end{aligned} \quad (5)$$

The external potential acting on the electrons is the Coulomb field of the nuclei

$$V_n(\mathbf{r}) = -k \sum_i^{N_e} \sum_I^{N_n} \frac{e^2 Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad (6)$$

and for the nuclei,

$$\begin{aligned} \hat{\mathcal{H}}_n \chi(\mathbf{R}) &= \left[ \sum_I^{N_n} \frac{\hat{P}_I^2}{2M_I} + \frac{k}{2} \sum_{I \neq J}^{N_n} \frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|} + \mathcal{E}_e(\mathbf{R}) \right] \chi(\mathbf{R}) \\ &= \mathcal{E}_n \chi(\mathbf{R}) \end{aligned} \quad (7)$$

Note the dependence of the nuclear energy  $\mathcal{E}_n$  on the electronic energy  $\mathcal{E}_e(\mathbf{R})$ . The electronic energy in the nuclear Hamiltonian is often called “the Born-Oppenheimer energy surface.” It acts as an “external” potential on the ions. It contains all of the effects of *instantaneous* electronic screening of the nuclear-nuclear Coulomb interaction. When making the adiabatic approximation, we are assuming the electrons instantly adjust to any change in the nuclear configuration. [Giustino’s review of the quantum field theory of electron-phonon coupling \[29\]](#) has a lot of discussion of the adiabatic approximation and corrections to it. [Refs. \[14, 67\] discuss it quite a bit too.](#)

We’ve simplified the problem quite a bit, but solving either one of these equations is still pretty much impossible because they are interacting systems. For now, suppose that we can, in principle, solve this system of equations. What does it tell us? A few examples come to mind in materials science. For instance, the derivative of the potential energies in the nuclear Hamiltonian are the *forces* acting on the nuclei. If we minimize these forces, we can determine the equilibrium structure of the material we are modelling. If the equilibrium structure is ordered, second derivatives are force-constants that can be used to model “phonons”, the quanta of lattice vibrations. These results can be used to calculate thermodynamics and other properties of crystals. Solving the electronic Hamiltonian at a given set of atomic coordinates gives us the electronic energy; i.e. the “band structure.” If we solve it at the equilibrium nuclear configuration, we can calculate thermodynamic and, to some extent, electronic transport quantities.

We need to figure out how to approach these equations in practice. We will return to problem of the nuclei later. For now, let’s focus on the electrons.

## 2.2 The Single-Particle Schrödinger’s Equation

The electronic Hamiltonian in eq. 5 is still insoluble. We face the same problem as in eq. 1. The electronic Coulomb potential is a two-particle operator and in the operator many-body formalism, these are non-linear operator equations; they *can not* be solved. The field of *many-body theory* is focused around the approximate solution of these equations within the framework of quantum field theory; see §7. The formalism of many-body physics is gnarly and the concepts can be difficult to grasp. So for now, let us take a step back.

Our plan of attack will be to try to reduce the many-problem with the two-particle operators into an effective single-particle theory. To be specific, we want to map the Hamiltonian in eq. 5 onto a set of single-particle Hamiltonians with an arbitrary external single-particle

potential. This will be directly accessible to the tools of *single-particle* quantum-mechanics<sup>3</sup> and we can more easily solve the effective theory.

There are varying degrees of sophistication to this and a few different types of theories can be derived. We want to find single-particle equations with all of the effects of the interactions placed into an effective potential. This might sound like “free lunch.” However, while the effective potentials will be single-particle type, they will depend explicitly on the wave-functions (the Hartree-Fock theory) or the density (density functional theories); such potentials are called “self-consistent.” Self-consistency is the price to be paid if we want to accurately include the effects of interactions in a single-particle theory. Before we dive into these theories, let’s warm up with a simpler example: the Hartree approximation.

### 2.2.1 The Hartree Approximation

The issue in solving eq. 5 lies in the Coulomb interaction, which is a two-particle operator in a second-quantized description. We want to replace it with an approximate single-particle operator. Re-write the electronic many-body Hamiltonian as

$$\hat{\mathcal{H}} = \sum_i^N \left( \frac{\hat{p}_i^2}{2m_e} + v_{ext}(\mathbf{r}_i) \right) + \frac{1}{2} \sum_{i \neq j}^N u(\mathbf{r}_i, \mathbf{r}_j) \quad (8)$$

For now, we will only talk about electrons so we drop the subscripts and don’t write nuclear coordinates. Moreover,  $v_{ext}(\mathbf{r}_i)$  can be any sensible *external* potential. The only restriction is that it can only depend on one electronic coordinate at a time. On the other hand,  $u(\mathbf{r}_i, \mathbf{r}_j)$  is a two-particle operator. It depends on two electronic coordinates, coupling particles. It doesn’t have to be the Coulomb interaction for now; it can be anything sensible in what follows.

Let’s re-write the interaction  $u(\mathbf{r}_i, \mathbf{r}_j)$  in terms of the electronic density operator  $\hat{n}(\mathbf{r}) = \sum_i^N \delta(\mathbf{r} - \mathbf{r}_i)$  [28]<sup>4</sup> First of all

$$u(\mathbf{r}_i, \mathbf{r}_j) = \int \int d\mathbf{r} d\mathbf{r}' \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) u(\mathbf{r}, \mathbf{r}')$$

If we sum this over all possible pairs of atoms, we have

$$\frac{1}{2} \sum_{i,j}^N u(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \hat{n}(\mathbf{r}) \hat{n}(\mathbf{r}') u(\mathbf{r}, \mathbf{r}')$$

This looks almost just like the two-particle potential in eq. 8, except it includes interactions between an electron and itself. Just subtract out the single-electron term:

$$\hat{U} \equiv \frac{1}{2} \sum_{i \neq j}^N u(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \hat{n}(\mathbf{r}) \hat{n}(\mathbf{r}') u(\mathbf{r}, \mathbf{r}') - \sum_i^N u(\mathbf{r}_i, \mathbf{r}_i)$$

<sup>3</sup> From now on, “quantum mechanics” will always mean single-particle; if there are more than one particles, we will use quantum field theory.

<sup>4</sup> Redo this derivation using the density *matrix* operator.

The last term is a constant and we can just cram it into the definition of the external potential.

Lets now rewrite the density as its mean plus fluctuations.  $\hat{n}(\mathbf{r}) = n(\mathbf{r}) + \delta\hat{n}(\mathbf{r})$ . The mean term is just the expectation value of the density  $n(\mathbf{r}) \equiv \langle \hat{n}(\mathbf{r}) \rangle$  and the fluctuation part is  $\delta\hat{n}(\mathbf{r}) = \hat{n}(\mathbf{r}) - n(\mathbf{r})$ . Stick this into the two-particle operator (ignoring the constant term).

$$\begin{aligned}\hat{U} &= \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' [n(\mathbf{r}) + \delta\hat{n}(\mathbf{r})][n(\mathbf{r}') + \delta\hat{n}(\mathbf{r}')] u(\mathbf{r}, \mathbf{r}') \\ &= \int d\mathbf{r} \hat{n}(\mathbf{r}) \left( \int d\mathbf{r}' n(\mathbf{r}') u(\mathbf{r}, \mathbf{r}') \right) \\ &\quad + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' [\delta\hat{n}(\mathbf{r})\delta\hat{n}(\mathbf{r}') - n(\mathbf{r})n(\mathbf{r}')] u(\mathbf{r}, \mathbf{r}')\end{aligned}\tag{9}$$

The last term in the last line is constant, so just like with the bonus part of eq. 8, we suppose we can just stick it into our external potential. For the remaining term (which is  $2^{nd}$  order in the fluctuations), let's suppose that the fluctuations are small and just throw it away. Define the *Hartree potential*

$$v_H(\mathbf{r}_i) = \int d\mathbf{r} n(\mathbf{r}) u(\mathbf{r}_i, \mathbf{r})\tag{10}$$

The name “Hartree potential” is usually used when  $u(\mathbf{r}_i, \mathbf{r})$  is the Coulomb interaction, but let's leave  $u(\mathbf{r}_i, \mathbf{r})$  unspecified for now. An important aspect of the Hartree potential is that it includes *self-interaction*: i.e. the electron feels the potential of its own density. This self-interaction leads to important errors in density functional theory. Anyway, lets rewrite eq. 8 as

$$\hat{\mathcal{H}}_H = \sum_i^N \left( \frac{\hat{p}_i^2}{2m_e} + v_{ext}(\mathbf{r}_i) + v_H(\mathbf{r}_i) \right).\tag{11}$$

We have removed the two-particle nature of the Coulomb interaction by coupling each electron to the *mean-field* of the electronic density. This kind of approximation is called a mean-field approximation. We replaced a non-linear problem with a self-consistent one. We threw away all effects of both exchange and dynamical correlation (i.e. the response of the density itself). This is about as simple an approximation that we can make to the true interacting many-body problem. It's a bad approximation because it neglects screening effects and other things, but it's a good starting point. Later on when discussing density functional theory, we will try to put exchange and correlation back in later while still keeping a single-particle description. But for now, we have made enough progress to discuss important qualitative features shared by the Hartree approximation, the Hartree-Fock method, and density functional theory.

Specifically, the methods for attacking any of these single-particle Hamiltonian are the same. Solving a single-particle equation like eq. 11 is mostly straightforward. We say *mostly* because the Hartree potential depends on the electronic density which is determined only after solving the Schrödinger's equation of the electrons. So this is a self-consistent-field (SCF) problem. The same situation will arise again when we study density functional theory, so it's worth discussing how we approach these problems in practice. But first, let's look at how *non-self-consistent* single-particle problems are solved in the first place.

### 2.2.2 The Variational Method

It's useful to phrase the single-particle problem in another way. We need to solve a single-particle Schrödinger's equation under an arbitrary (but sensible) external potential. We will only focus on time-independent potentials here, so we will specialize to the time-independent Schrödinger's equation (TISE). The TISE in Dirac notation is

$$\hat{\mathcal{H}}|\psi_\alpha\rangle = \epsilon_\alpha|\psi_\alpha\rangle \quad (12)$$

i.e. an eigenvalue problem. We are using lower-case Greek letters for single-particle wavefunctions.  $\hat{\mathcal{H}}$  is a single-particle operator and the eigenvectors are single-particle states. Our goal is to find the eigenvalues and eigenvectors.

It turns out that direct numerical integration isn't really practical in most cases<sup>5</sup>. So suppose instead that we do the following. Let  $|\psi\rangle$  be some arbitrary trial state that we can somehow vary continuously. The expectation value of  $\hat{\mathcal{H}}$  with respect to this function is

$$\langle\hat{\mathcal{H}}\rangle = \frac{\langle\psi|\hat{\mathcal{H}}|\psi\rangle}{\langle\psi|\psi\rangle}$$

i.e.  $\langle\hat{\mathcal{H}}\rangle$  is the energy of the trial state. We don't want the normalization to change, so we impose the constraint that this expectation value is normalized by dividing by the overlap. On physical grounds, we want to find the state that minimizes the energy. So we need to find the state that minimizes the expectation value. Let the trial state  $|\psi + \delta\psi\rangle = |\psi\rangle + |\delta\psi\rangle$  include variations around the true solution,  $|\psi\rangle$ . We expect the variation  $|\delta\psi\rangle$  to be small, but it is allowed to be arbitrary. The new expectation value with the trial state is

$$\langle\hat{\mathcal{H}}\rangle + \delta\langle\hat{\mathcal{H}}\rangle = \frac{\langle\psi + \delta\psi|\hat{\mathcal{H}}|\psi + \delta\psi\rangle}{\langle\psi + \delta\psi|\psi + \delta\psi\rangle} \approx \frac{\langle\psi|\hat{\mathcal{H}}|\psi\rangle + \langle\delta\psi|\hat{\mathcal{H}}|\psi\rangle + \langle\psi|\hat{\mathcal{H}}|\delta\psi\rangle}{\langle\psi|\psi\rangle + \langle\delta\psi|\psi\rangle + \langle\psi|\delta\psi\rangle}$$

We ignore second order terms, since they are small. Use the expansion  $(1+x)^{-1} \approx 1-x$  for small  $x$  to make the replacement

$$\langle\psi|\psi\rangle^{-1} \left[ 1 + \frac{\langle\delta\psi|\psi\rangle + \langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} \right]^{-1} \approx \langle\psi|\psi\rangle^{-1} \left[ 1 - \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} \right]$$

Plug this in and drop second order terms again

$$\delta\langle\hat{\mathcal{H}}\rangle = \frac{\langle\delta\psi|\hat{\mathcal{H}}|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|\hat{\mathcal{H}}|\delta\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\psi|\hat{\mathcal{H}}|\psi\rangle}{\langle\psi|\psi\rangle} \left[ \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} \right]$$

We are looking for the minimum of  $\langle\hat{\mathcal{H}}\rangle$  with respect to variation of  $|\psi\rangle$ . Just like in ordinary calculus, the minimum is an extrema and  $\delta\langle\hat{\mathcal{H}}\rangle \equiv 0$ . Then

$$\langle\delta\psi|\hat{\mathcal{H}} - \langle\hat{\mathcal{H}}|\psi\rangle + \langle\psi|\hat{\mathcal{H}} - \langle\hat{\mathcal{H}}|\delta\psi\rangle \equiv 0$$

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<sup>5</sup> These methods are currently under active research []



Now in general  $|\delta\psi\rangle$  is complex. It has two components that can be varied independently; the real and imaginary parts. Equivalently,  $|\delta\psi\rangle$  and  $|\delta\psi\rangle^\dagger \equiv \langle\delta\psi|$  can be varied independently. So, considering the arbitrariness of the variation  $|\delta\psi\rangle$ , we find that

$$\hat{\mathcal{H}}|\psi\rangle = \langle\hat{\mathcal{H}}|\psi\rangle$$

This proves that states that *extremizes*  $\langle\hat{\mathcal{H}}\rangle \equiv \mathcal{E}$  are solutions of the TISE.

In words, the variational method can be used to solve the TISE in the following way: we make a guess for the wave-function that depends on parameters. We calculate  $\langle\hat{\mathcal{H}}\rangle$  for a given set of parameters and vary them until the energy is extremized. In math, we calculate the following quantity

$$\mathcal{E}(\alpha_1, \dots, \alpha_n) \equiv \langle\hat{\mathcal{H}}\rangle = \int d\mathbf{r} \psi^*(\mathbf{r}; \alpha_1, \dots, \alpha_n) \hat{\mathcal{H}} \psi(\mathbf{r}; \alpha_1, \dots, \alpha_n) \quad (13)$$

and look for the set  $\{\alpha_1, \dots, \alpha_n\}$  that satisfies

$$\frac{\partial \mathcal{E}}{\partial \alpha_1} = \dots = \frac{\partial \mathcal{E}}{\partial \alpha_n} = 0$$

Now let's see what this all tells us. Call  $\epsilon_0 \equiv \mathcal{E}_0$  the ground-state energy. The eigenvectors in the TISE eq. 12 are a complete set, so we can expand our *trial state* as  $|\psi\rangle = \sum_{\alpha} c_{\alpha} |\psi_{\alpha}\rangle$ . The expectation value is

$$\mathcal{E} = \langle\psi|\hat{\mathcal{H}}|\psi\rangle = \frac{\sum_{\alpha} |c_{\alpha}|^2 \epsilon_{\alpha}}{\sum_{\alpha} |c_{\alpha}|^2} = \mathcal{E}_0 + \frac{\sum_{\alpha} |c_{\alpha}|^2 (\epsilon_{\alpha} - \mathcal{E}_0)}{\sum_{\alpha} |c_{\alpha}|^2}$$

Clearly  $\epsilon_{\alpha} \geq \mathcal{E}_0$ , where it is a strict inequality if the ground-state is non-degenerate. So the whole second term is a positive number (or zero). Lets call it  $\Delta\mathcal{E}$ . Then it turns out that

$$\mathcal{E} \geq \mathcal{E}_0 + \Delta\mathcal{E} \quad (14)$$

The variational method puts an upper bound on the true ground-state energy, a neat result. If we can't solve a particular problem, we can approximate the solution and try to get as close as possible. In practice, we usually pick a set of functions, called the *basis*, and use linear combinations of them as trial solutions.

### 2.2.3 The Secular Equation

We have convinced ourselves that we can approximate the solution to the TISE, but we really still haven't said *how* to solve the problem.

We can solve eq. 12 by first choosing a variational basis and expanding the eigenvectors (the “kets”) in that basis. The variational method finds the ground-state, so we can drop the subscript and assume the eigenvector we are solving for is always the ground-state. Let the new basis vectors be called  $|\phi_{\alpha}\rangle$ . In the new basis, the kets are

$$|\psi\rangle = \sum_{\alpha} c_{\alpha} |\phi_{\alpha}\rangle$$

where  $c_\alpha$  are complex expansion coefficients and the sum runs over all basis vectors: possibly infinitely many. The TISE becomes

$$\sum_{\alpha} c_{\alpha} \hat{\mathcal{H}} |\phi_{\alpha}\rangle = \sum_{\alpha} c_{\alpha} \mathcal{E} |\phi_{\alpha}\rangle$$

The expectation value in eq. 13 is

$$\sum_{\alpha, \beta} c_{\alpha} c_{\beta}^* \langle \phi_{\beta} | \hat{\mathcal{H}} | \phi_{\alpha} \rangle = \sum_{\alpha, \beta} c_{\alpha} c_{\beta}^* \mathcal{E} \langle \phi_{\beta} | \phi_{\alpha} \rangle$$

It is common to write the matrix-elements as  $\langle \phi_{\alpha} | \hat{\mathcal{H}} | \phi_{\beta} \rangle \equiv \mathcal{H}_{\alpha, \beta}$  and  $\langle \phi_{\alpha} | \phi_{\beta} \rangle \equiv S_{\alpha, \beta}$ . We dropped the “hat” on  $\mathcal{H}$  to emphasize that this is just a number. The elements  $S_{\alpha, \beta}$  are called orbital overlaps and the matrix of elements  $\hat{\mathcal{S}}$  is the overlap operator. Note that if the basis functions are orthonormal (e.g. suitably chosen plane-waves), the overlap operator is just the identity matrix.

The coefficients  $c_{\alpha}$  are the variational parameters. If we want to calculate the wave-function, we minimize with respect to the complex-conjugate coefficients (i.e. the variation is  $\langle \delta\psi |$ ). The derivative of eq. 13 is

$$\sum_{\alpha} (\mathcal{H}_{\alpha, \beta} - \mathcal{E} S_{\alpha, \beta}) c_{\alpha} \quad (15)$$

After staring carefully at eq. 15 for a minute, we recognize this is the Schrödinger’s equation in matrix notation:

$$\hat{\mathcal{H}} \mathbf{c} = \mathcal{E} \hat{\mathcal{S}} \mathbf{c} \quad (16)$$

where we introduced  $\mathbf{c}$  as the column matrix of expansion coefficients. So we’ve shown that the TISE can be represented as an auxiliary TISE for the variational basis orbitals. But we have written it in the secular form of eq. 16 which we know how to solve: by diagonalization. The eigenvectors are stationary-states of the original TISE. The lowest eigenvalue is always greater than or equal to the ground-state energy. If we use a complete set of basis functions, e.g. plane-waves, we can in-principle calculate the exact solution. However, we would have to diagonalize an infinite dimensional matrix... which we can’t do.

What if we just truncate the basis-set? Eq. 15 still holds and can be diagonalized on a computer. It’s a generalized eigenvalue problem, but know how to solve those too (at worst, it is just diagonalizing two matrices instead of one: see §3.3 in Thijssen [71]). The method laid out in this section is how the single-particle problem is usually solved in modern computational condensed matter physics. The discussion was pretty general; in practice, we still have to choose a specific basis and figure out how to calculate the matrix elements. The basis functions can be plane-waves, localized atomic-like orbitals, or linear-combinations of atomic-orbitals (their generalization in solids). Another other options is using tabulated numerical functions. There are plenty of reasons to choose one-or-the-other, but that is out of scope of the present discussion.

### 2.2.4 The Self-Consistent-Field Method

We are looking for the solutions of the Hartree Hamiltonian in eq. 11. The difficulty is that the Hamiltonian depends explicitly on the density. Let's generalize from the Hartree approximation and study any Hamiltonian  $\hat{\mathcal{H}}[n(\mathbf{r})] = \hat{T} + \hat{V}[n(\mathbf{r})]$  in which the potential depends explicitly on the electronic density. The density is calculated from the wave-functions, so the solution, in a sense, depends on itself. We say that the solution has to be *self-consistent*.

We can still express the TISE as an eigenvalue problem

$$\hat{\mathcal{H}}[n(\mathbf{r})]\psi_\alpha(\mathbf{r}) = \epsilon_\alpha\psi_\alpha(\mathbf{r})$$

The Hamiltonian depends on the solutions  $\psi_\alpha(\mathbf{r})$  (or more precisely on the density which depends on the solutions) so it's a self-consistent problem. Since the potential depends on the solution, it is called a self-consistent potential. The method to solve it is called the self-consistent field (SCF) method [28, 52, 71].

In the Hartree approximation, the self-consistent potential is the Hartree potential. But we don't need to be specific right now. All that matters is that the potential *can* be calculated once the density is known. The electronic number-density is

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 f(\epsilon_i) \quad (17)$$

The sum runs over all basis functions. The *charge*-density is  $\rho(\mathbf{r}) = en(\mathbf{r})$ . The number  $f(\epsilon)$  is the “occupation” of the single-particle state. This is included for physical reasons; in equilibrium, only the lowest energy states are occupied (of course each state can, at most, hold only one electron). At zero temperature, it is convenient to use a step function:  $f(\epsilon) = \theta(\epsilon_F - \epsilon)$  with  $\epsilon_F$  the *Fermi-energy*. At finite temperature, it makes more sense to use the Fermi-Dirac distribution function:

$$f(\epsilon) = \left[ \exp\left(\frac{\epsilon - \epsilon_F}{k_B T}\right) + 1 \right]^{-1} \quad (18)$$

$k_B$  is Boltzmann's constant and  $T$  is the temperature. The Fermi-energy  $\epsilon_F$  is determined from [71]<sup>6</sup>

$$\int d\mathbf{r} n(\mathbf{r}) = \sum_i f(\epsilon_i) = N \quad (19)$$

i.e. the total number of occupied single-particle states must equal the number of particles.  $\epsilon_F$  is the energy of the highest occupied state that satisfies this requirement. Now for the SCF method.

For now, let's just state it in words.

1. We make a guess for the initial orbitals,  $\psi_\alpha(\mathbf{r})$ . In a condensed matter setting, a reasonable guess is atomic orbitals.

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<sup>6</sup> see [1] for a technical implementation

2. We then calculate the density and the potential and solve the secular problem. The solutions  $\psi_\alpha(\mathbf{r})$  determine the density.
3. For the solution to make sense, the input and output densities had better be identical. So we inspect the differences between the input and output densities.
4. If they agree within some prescribed value, then all is good and we consider the problem solved: the final  $\{\psi_\alpha(\mathbf{r})\}$  and  $\{\epsilon_\alpha\}$  are the solutions.
5. If they don't agree, we make a new guess for the density and try again. The process is iterated until "self-consistency" is reached.

There are many ways to "guess again." Usually some of the old density is mixed with the new and the mixture is used as the input density for the next SCF step. Since each step involves diagonalizing a (usually large) matrix, it is essential to reach self-consistency as quickly as possible. The method for "mixing" the densities is crucial. **We will study mixing in detail later.**

## 2.3 The Hartree-Fock Approximation

The Hartree-Fock approximation will turn out to look like an extension to the Hartree approximation, but the derivation looks quite different. The essence of the Hartree-Fock approximation is to assume that the many-body wave-function can be written as a *single* Slater determinant [28, 71]. This is called the *independent particle approximation*. Before moving on, we want some intuition for what physics the independent particle approximation is neglecting. In the independent-particle approximation, the wave-function is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \sim \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \cdots \psi_N(\mathbf{r}_N)$$

i.e. a product of single-particle wave-functions. The one-particle wave-functions are assumed orthonormal (this isn't a requirement, but is for simplicity). The probability density

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \equiv (|\psi_1(\mathbf{r}_1)|^2 d\mathbf{r}_1)(|\psi_2(\mathbf{r}_2)|^2 d\mathbf{r}_2) \cdots (|\psi_N(\mathbf{r}_N)|^2 d\mathbf{r}_N)$$

is just the product of single-particle probabilities. The fact is, a variation in the "probability" of a particular particle doesn't explicitly affect the probability of another particle. Clearly this isn't the case in a full many-body description. The physics we are neglecting can be called "correlation" [71]. An independent-particle many-body wave-function can be called "uncorrelated."

Alright, so the first approximation is to assume that the many-particle wave-function can be written as a product of single-particle states. We can still enforce *some* correct physics by demanding that the wave function satisfies the correct exchange statistics:

$$\hat{\mathcal{P}}\Psi(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N) = \pm \Psi(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N)$$

where the  $+$  is for Bosons and  $-$  is for Fermions.  $\hat{\mathcal{P}}$  is the permutation operator which permutes a pair of particle's spin and position coordinates. We will almost exclusively look

at electrons which are spin-1/2. They are Fermions, so the wave function has to be *anti*-symmetric with respect to particle exchange (see §7). Let's let  $\mathbf{x}_i \equiv \{\mathbf{r}_i, \sigma_i\}$  be a composite coordinate for position and spin.  $\hat{\mathcal{P}}$  only acts on the coordinates and leaves orbital indices alone. If it acted on both coordinates and indices, the wave-function wouldn't change. Alternatively, it could only act only on indices, but we define it to act on coordinates.

We want a wave-function that satisfies the anti-symmetry requirement for identical particles. A simple product of independent-particle wave-functions doesn't work, but it turns out that the following linear combination does the trick:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = (N!)^{-1/2} \sum_{\mathcal{P}} (-1)^{\mathcal{P}} \hat{\mathcal{P}} \psi_1(\mathbf{x}_1) \psi_2(\mathbf{x}_2) \cdots \psi_N(\mathbf{x}_N) \quad (20)$$

The sum runs over all possible permutations. The factor  $(-1)^{\mathcal{P}}$  is 1 or  $-1$  depending on whether an even or odd number of particles has been exchanged respectively.  $\psi(\mathbf{x}) \equiv \psi(\mathbf{r})\alpha(\sigma)$  are “spin-orbitals”. i.e. every wave-function  $\psi(\mathbf{r})$  comes in both spin-up and spin-down flavors. The wave-function in eq. 20 is usually called a *Slater determinant* after physicist John C. Slater and because it can be represented as a determinant. In a *non-interacting* many-particle problem, eq. 20 is an exact wave-function and the independent-particle approximation is exact. But for interacting Hamiltonians, it is an approximation. Still, we saw earlier that we can use Slater determinants as a variational basis to approximate the true solution to the interacting problem.

Let's study this wave-function a little. Since the Hartree-Fock approximation won't be of particular importance later on, we can do it hand-wavey. Details are in refs. [28] and [71] and in exercise 4.3 in ref. [71]. The probability density for an electron to be at position  $\mathbf{r}_1$  and another simultaneously at  $\mathbf{r}_2$  is

$$\begin{aligned} n(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{\sigma_1, \dots, \sigma_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 \propto \\ &\sum_{i,j} \sum_{\sigma_i, \sigma_j} (|\psi_i(\mathbf{r}_1)|^2 |\psi_j(\mathbf{r}_2)|^2 - \psi_i^*(\mathbf{r}_1) \psi_i(\mathbf{r}_2) \psi_j^*(\mathbf{r}_2) \psi_j(\mathbf{r}_1)) \end{aligned} \quad (21)$$

We are ignoring the combinatorial normalization factor. There are two distinct cases:  $\sigma_1 = \sigma_2$  and  $\sigma_1 = -\sigma_2$ . If the electrons have opposite spins,  $\alpha_i^\dagger(\sigma)\alpha_i(-\sigma) \equiv 0$  in the second term and it vanishes. The pair-probability for electrons with different spins is the same as the single-particle probability for two electrons. Opposite spins are “uncorrelated.” If the spins are the same (“parallel”), the second-term doesn't vanish. However, for parallel spins, if  $\mathbf{r}_1 = \mathbf{r}_2$  the pair-probability vanishes. This is the familiar Pauli exclusion principle. The consequence is that the probability of finding two electrons in the same orbital with the same spin at the same position is identically zero: parallel spins are “correlated,” though this type of correlation is usually just called “exchange” and is distinct from other correlation phenomena such as screening. Exchange is responsible for most magnetism observed in condensed matter [28].

Let's calculate the matrix elements of eq. 8.

$$\langle \Psi | \hat{\mathcal{H}} | \Psi \rangle = \langle \Psi | \hat{V}(\mathbf{r}) | \Psi \rangle + \langle \Psi | \hat{U}(\mathbf{r}, \mathbf{r}') | \Psi \rangle$$

This a sum of one-particle and two-particle matrix elements. The one-particle term is

$$\langle \Psi | \hat{V}(\mathbf{r}) | \Psi \rangle = \sum_i \langle \Psi | v(\mathbf{r}_i) | \Psi \rangle = \sum_i \langle \psi_i | v(\mathbf{r}_i) | \psi_i \rangle$$

i.e. it is just the sum of one-particle matrix elements. Overlaps between spin-orbitals (i.e. states with a composite coordinate  $\mathbf{x} = \{\mathbf{r}, \sigma\}$ ) is integration over space and a sum over spins. The matrix element of the two-particle operator is

$$\begin{aligned} \langle \Psi | \hat{U}(\mathbf{r}, \mathbf{r}') | \Psi \rangle = \\ \frac{1}{2} \sum_{i,j} \sum_{\sigma_i, \sigma_j} \int d\mathbf{r}_i d\mathbf{r}_j [\psi_i^*(\mathbf{r}_i, \sigma_i) \psi_j^*(\mathbf{r}_j, \sigma_j) u(\mathbf{r}_i, \mathbf{r}_j) \psi_i(\mathbf{r}_i, \sigma_i) \psi_j(\mathbf{r}_j, \sigma_j) \\ - \psi_i^*(\mathbf{r}_i, \sigma_i) \psi_j^*(\mathbf{r}_j, \sigma_j) u(\mathbf{r}_i, \mathbf{r}_j) \psi_i(\mathbf{r}_j, \sigma_i) \psi_j(\mathbf{r}_i, \sigma_j)] \end{aligned} \quad (22)$$

Interestingly, if  $i \equiv j$ , the matrix-element vanishes and there is no self-interaction like there was in the Hartree approximation.

The Hamiltonian matrix element is a functional of the orbitals. We would like to apply the variational principle and minimize the expectation value with respect to the single-particle functions. Ultimately, we want a secular equation for the single-particle states since we know how to solve those (diagonalization). But the variational basis functions are Slater determinants of the single-particle functions, so the simple approach in §2.2.2 won't be easy to apply (try it and see). In our earlier study of the variational method, we satisfied the requirement that solutions of the TISE are orthonormal by explicitly normalizing the expectation value. The other way to impose the constraint is with Lagrange multipliers: this is the way to go in this problem [28, 71].

There are lots of messy steps that I don't want to go through, so I will just quote the answer. The Hartree-Fock equations are

$$\hat{\mathcal{F}}\psi_i(\mathbf{x}) = \left[ v(\mathbf{r}) + v_H(\mathbf{r}) - \hat{K}(\mathbf{x}) \right] \psi_i(\mathbf{x}) = \epsilon_i \psi_i(\mathbf{x}) \quad (23)$$

$\hat{\mathcal{F}}$  is called the “Fock operator.”  $v(\mathbf{r})$  is just the typical single-particle potential we have looked at many times: it is usually just the sum of kinetic-energy and external potentials acting only on one particle.  $v_H(\mathbf{r})$  is just the Hartree potential from earlier:

$$v_H(\mathbf{r}) = \int d\mathbf{r}' n(\mathbf{r}') u(\mathbf{r}, \mathbf{r}')$$

The last operator,  $\hat{K}$ , is called the exchange operator. It is essentially the Hartree potential with the particle swapped with another inside the density. It is a non-local operator whose action on a spin-orbital is

$$\hat{K}(\mathbf{x})\psi_i(\mathbf{x}) = \sum_j' \sum_{\sigma_j} \int d\mathbf{r}_j \psi_j^*(\mathbf{x}_j) \psi_i(\mathbf{x}_j) u(\mathbf{r}, \mathbf{r}_j) \psi_j(\mathbf{x}) \quad (24)$$

The prime on the sum is to indicate that it is only over *occupied* orbitals, though in practice the occupations are set according to e.g. the Fermi-Dirac function and the sum runs over all

orbitals. Clearly this is another example of a SCF problem. The Hartree potential depends on the density while the exchange operator depends explicitly on the orbitals.

Eqs. 23 represent an auxiliary set of equations whose solutions, when combined into the Slater determinant in eq. 20, minimize the energy expectation value. Eq. 23 can be solved by expanding the  $|\psi_i\rangle$  in a basis and diagonalizing. The eigenvalues  $\epsilon_i$  are not “energies.” They are Lagrange multipliers needed to satisfy the orthonormality constraint. Still, they are related to the electronic ground state energy. Let’s see how. Calculate the expectation value of the Hamiltonian

$$\begin{aligned}\langle\Psi|\hat{\mathcal{H}}|\Psi\rangle &= \sum_i \langle\psi_i|v(\mathbf{r}_i) + \frac{1}{2} \left( v_H(\mathbf{r}_i) - \hat{K}(\mathbf{x}_i) \right) |\psi_i\rangle \\ &= \frac{1}{2} \sum_i \left( \langle\psi_i|v(\mathbf{r}_i)|\psi_i\rangle + \langle\psi_i|\hat{\mathcal{F}}|\psi_i\rangle \right)\end{aligned}$$

Once the solutions  $|\psi_i\rangle$  are known, the single-particle potential matrix elements are easy to calculate. So the ground-state energy in the Hartree-Fock approximation is

$$\mathcal{E}_{HF} = \frac{1}{2} \sum_i \left( \langle\psi_i|v(\mathbf{r}_i)|\psi_i\rangle + \epsilon_i \right) \quad (25)$$

Let’s connect back to the Born-Oppenheimer Hamiltonian eq. 5. The external potential would be the Coulomb field of the nuclei  $V_n(\mathbf{R})$ .  $\mathcal{E}_{HF}(\mathbf{R})$  is an approximation to the ground-state electronic energy for a given configuration of the nuclei.

The non-local nature of the exchange operator makes it difficult to work with; e.g. it corresponds to “hopping” arbitrary distances in tight-binding [28]. Moreover, the Hartree-Fock approximation neglects all screening (by writing the wave-function as a Slater determinant) and naturally performs poorly for many correlated-electron problems in condensed matter.

## 2.4 Density Functional Theory

In §2.3, we found a set of equations that approximate the solution to the ground-state energy of the interacting problem. The Hartree-Fock approximation accurately includes exchange effects, but severely neglects correlation. Moreover, the Hartree-Fock equations involve a non-local operator that is a funny thing to handle in practice. In particular, it is hard to represent non-local operators in extended systems (e.g. solids). To get around these issues, we need to try again. Let’s study density functional theory (DFT) [27, 28, 52, 71]. Actually, it turns out that DFT is not an approximation: it is a reformulation of the many-body problem in terms of the charge density instead of the wave-functions.

It is many pages ago that we last wrote down the Hamiltonian we are trying to solve, so let’s repeat it here:

$$\hat{\mathcal{H}} = \sum_i^N \frac{\hat{p}_i^2}{2m_e} + \sum_i^N v_{ext}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j}^N u(\mathbf{r}_i, \mathbf{r}_j) \equiv \hat{T} + \hat{V} + \hat{U} \quad (26)$$

In condensed matter, the kinetic-energy and two-particle operators,  $\hat{T}$  and  $\hat{U}$  respectively, are the same regardless of what external potential,  $\hat{V}$ , we might be exposing the electrons

to. The form of the Hamiltonian in different systems differs only by the external potential. Our method of attack is to study the most general external potential possible and try to solve the problem once-and-for-all.

The first step is to note that since the external potential is a one-particle operator that can be written as

$$\hat{V} = \sum_i v(\mathbf{r}_i) = \sum_i \int d\mathbf{r} \delta(\mathbf{r} - \mathbf{r}_i) v(\mathbf{r}) = \int d\mathbf{r} \hat{n}(\mathbf{r}) v(\mathbf{r})$$

where we substitute the density operator  $\hat{n}(\mathbf{r})$  we encountered earlier. We have dropped the subscript on  $v_{ext}$  to ease notation.  $v$  should be assumed external for now. The expectation value of the external potential

$$\langle \Psi | \hat{V} | \Psi \rangle = \int d\mathbf{r} \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle v(\mathbf{r}) = \int d\mathbf{r} n(\mathbf{r}) v(\mathbf{r})$$

depends only on the expectation value of the density,  $n(\mathbf{r})$ . We haven't made any assumptions about  $|\Psi\rangle$  yet. It might as well be the exact ground-state solution to the many-body Hamiltonian in eq. 26. So we have found that the potential  $\langle \Psi | \hat{V} | \Psi \rangle \equiv V[n(\mathbf{r})]$  can be represented as a *functional* of the density. Inspired by this, we want to reformulate the expectation value of the Hamiltonian as a functional of the density. Can this be done? It turns out that it can, as proved in two theorems by Hohenberg and Kohn in the 1960's. These theorems essentially prove that the exact many-problem can be expressed in terms of a unique density and that the density minimizes the ground-state energy. Let us lazily prove the Hohenberg-Kohn theorems. Our discussion follows Girvin and Yang [28].

### 2.4.1 The Hohenberg-Kohn Theorems

We first postulate that the ground-state energy is a functional of the density. In math

$$\mathcal{E}[n(\mathbf{r})] \equiv \mathcal{H}[n(\mathbf{r})] = \langle \Psi_0 | \hat{\mathcal{H}} | \Psi_0 \rangle \quad (27)$$

where  $|\Psi_0\rangle$  is the ground-state solution. We assume the ground-state is not degenerate. The density is  $n(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle$ . We are looking for a way to formulate the ground-state energy as a functional of the density. If the energy functional and density are in one-to-one correspondence, we can (in principle) map the ground-state energy onto a functional of the density. Obviously if we are given  $|\Psi_0\rangle$ , there is only one  $n(\mathbf{r})$ . What is *not* obvious is that, given a  $n(\mathbf{r})$  there is only one  $|\Psi_0\rangle$ . This is what we need to prove. If it's true, there is a one-to-one map between the ground-state energy and the density and the postulate in eq. 27 is true.

The **1<sup>st</sup> Hohenberg-Kohn theorem** proves that the density  $n(\mathbf{r})$  and the ground-state solution  $|\Psi_0\rangle$  are in one-to-one correspondence. In other words, two different wavefunctions can't result in the same density. The proof is by *reductio ad absurdum*. Suppose that  $|\Psi_1\rangle$  and  $|\Psi_2\rangle$  are ground-states of Hamiltonians with two different external potentials  $V_1[n(\mathbf{r})]$  and  $V_2[n(\mathbf{r})]$ , but that  $\langle \Psi_1 | \hat{n}(\mathbf{r}) | \Psi_1 \rangle = \langle \Psi_2 | \hat{n}(\mathbf{r}) | \Psi_2 \rangle$ . The rest of the Hamiltonian is identical between them. The energies are  $\mathcal{E}_1 = \langle \Psi_1 | \hat{\mathcal{H}}_1 | \Psi_1 \rangle$  and  $\mathcal{E}_2 = \langle \Psi_2 | \hat{\mathcal{H}}_2 | \Psi_2 \rangle$ . Earlier



we proved that variational solutions are always above the true ground-state energy. Then  $\mathcal{E}_2 < \langle \Psi_1 | \hat{\mathcal{H}}_2 | \Psi_1 \rangle$ .

$$\begin{aligned} \mathcal{E}_2 &< \langle \Psi_1 | \hat{\mathcal{H}}_1 | \Psi_1 \rangle + \langle \Psi_1 | \hat{\mathcal{H}}_2 - \hat{\mathcal{H}}_1 | \Psi_1 \rangle \\ &< \mathcal{E}_1 + \langle \Psi_1 | \hat{V}_2 - \hat{V}_1 | \Psi_1 \rangle \end{aligned}$$

Identical reasoning results in

$$\mathcal{E}_1 < \mathcal{E}_2 + \langle \Psi_2 | \hat{V}_1 - \hat{V}_2 | \Psi_2 \rangle$$

Adding these two, together

$$\mathcal{E}_1 + \mathcal{E}_2 < \mathcal{E}_1 + \mathcal{E}_2 + \langle \Psi_2 | \hat{V}_1 - \hat{V}_2 | \Psi_2 \rangle + \langle \Psi_1 | \hat{V}_2 - \hat{V}_1 | \Psi_1 \rangle$$

The last two terms become

$$\begin{aligned} &\langle \Psi_2 | \hat{V}_1 - \hat{V}_2 | \Psi_2 \rangle + \langle \Psi_1 | \hat{V}_2 - \hat{V}_1 | \Psi_1 \rangle \\ &= \int d\mathbf{r} n(\mathbf{r}) (v_1(\mathbf{r}) - v_1(\mathbf{r}) + v_2(\mathbf{r}) - v_2(\mathbf{r})) = 0 \end{aligned}$$

and we find

$$\mathcal{E}_1 + \mathcal{E}_2 < \mathcal{E}_1 + \mathcal{E}_2$$

which is a logical contradiction. Thus, we have proved that  $\langle \Psi_1 | \hat{n}(\mathbf{r}) | \Psi_1 \rangle \neq \langle \Psi_2 | \hat{n}(\mathbf{r}) | \Psi_2 \rangle$ , where  $|\Psi_1\rangle$  and  $|\Psi_2\rangle$  are solutions to Schrödinger's equations that differ only by their external potentials. Two different wave-functions cannot generate the same density. There is only one  $|\Psi_0\rangle$  that solves a particular Hamiltonian and it solves only that one.

The **2<sup>nd</sup> Hohenberg-Kohn theorem** proves that  $n(\mathbf{r})$  calculated from the ground-state solution  $|\Psi_0\rangle$  minimizes the energy functional

$$\mathcal{E}[n(\mathbf{r})] = \langle \Psi_0 | \hat{\mathcal{H}} | \Psi_0 \rangle \quad (28)$$

$$= \mathcal{E}_U[n(\mathbf{r})] + \int d\mathbf{r} n(\mathbf{r}) v(\mathbf{r}) \quad (29)$$

The “universal functional” is completely independent of the external potential:

$$\mathcal{E}_U[n(\mathbf{r})] = \langle \Psi_0 | \hat{T} + \hat{U} | \Psi_0 \rangle$$

The **1<sup>st</sup> Hohenberg-Kohn theorem** essential proves that the universal functional exists. How to calculate it is unknown, but we can forget about that for now. Let's suppose that  $n_1(\mathbf{r})$  and  $|\Psi_1\rangle$  are the solution and density of some other ground-state. By virtue of the variational approximation,

$$\mathcal{E}[n_1(\mathbf{r})] = \langle \Psi_1 | \hat{\mathcal{H}} | \Psi_1 \rangle > \mathcal{E}[n(\mathbf{r})]$$

If  $|\Psi_1\rangle$  is not the ground-state solution, then its density doesn't minimize the energy-functional. The smallest value of the energy functional is then for  $n(\mathbf{r})$ , which is in one-to-one

correspondence with  $|\Psi_0\rangle$ , the ground-state solution. It's clear that the simplification of the many-body problem provided by the Hohenberg-Kohn theorems is enormous. We went from solving for a  $3N$  dimensional complex valued wave-function to solving for a 3 dimensional real scalar function. Still, there is no free lunch: the wave-function  $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$  is still a  $3N$  dimensional quantity and how to calculate it from the density is unknown. This theoretical framework is called density functional theory. Virtually all “ab-initio” calculations in materials science today are done in DFT and the success of this method is exemplified by the fact that Walter Kohn was awarded the Nobel prize in chemistry for his work on DFT.

### 2.4.2 The Kohn-Sham Equations

So far, the discussion was very general and we haven't really said how to solve a problem in practice. Moreover, we mentioned that we don't even know what the universal functional  $\mathcal{E}_U[n(\mathbf{r})]$  is. All we know is that it exists. How do we make progress? First of all, we will separate out all the parts of  $\mathcal{E}_U[n(\mathbf{r})]$  that we can calculate. Then we will approximate the rest of it. Hopefully the things we can calculate will be a large fraction of the total energy, so any errors in “the rest of it” will be small. Second, we want to do the same thing we did in the Hartree and Hartree-Fock approximations: recast the problem as an auxiliary set of effective single-particle equations. We do this because we know how to solve single-particle equations. In DFT, these are the *Kohn-Sham equations* [27, 28, 52, 71]

We start by ignoring interactions. It turns out that the even for non-interacting systems, we don't know how to write down  $\mathcal{E}_U[n(\mathbf{r})]$  directly [71]. But we do know how to calculate the ground-state energy  $\mathcal{E}[n(\mathbf{r})]$  for non-interacting particles. The ground-state wave-function is a Slater determinant of single-particle wave-functions  $\psi_{i,\sigma}(\mathbf{r})$ , eq. 20.  $i$  is the orbital index and  $\sigma$  is the spin index. The density is

$$n(\mathbf{r}) = \sum_{i,\sigma} f_{i,\sigma} |\psi_{i,\sigma}(\mathbf{r})|^2 \quad (30)$$

Ignoring interactions, the Hamiltonian only has single-particle operators and the exact energy functional is

$$\mathcal{E}[n(\mathbf{r})] = T_s[n(\mathbf{r})] + \int d\mathbf{r} n(\mathbf{r}) v(\mathbf{r}) = \sum_{i,\sigma} f_{i,\sigma} \langle \psi_{i,\sigma} | -\frac{\hbar^2}{2m_e} \nabla_i^2 + v(\mathbf{r}_i) | \psi_{i,\sigma} \rangle$$

$T_s[n(\mathbf{r})]$  is the single-particle kinetic energy functional. The external potential terms on both sides are exactly the same and we find

$$T_s[n(\mathbf{r})] = -\frac{\hbar^2}{2m_e} \sum_{i,\sigma} f_{i,\sigma} \langle \psi_{i,\sigma} | \nabla_i^2 | \psi_{i,\sigma} \rangle$$

This is the exact *non-interacting* kinetic energy functional for a particular density  $n(\mathbf{r})$ . Now back to the interacting problem. We want to write down all the interactions that we know how to calculate as our best guess to the true many-body energy functional. We can't write the ground-state wave-function  $\Psi_0(\mathbf{x}_1, \dots, \mathbf{x}_N)$  as a Slater determinant, but we are still free to expand the density in a basis: we use the same density in eq. 30. The spin-orbitals

used to expand the density are not necessarily solutions of the Schrödinger's equation. They are auxiliary functions called “Kohn-Sham orbitals” and turn out to be solutions of the Kohn-Sham equations. Now let's put together our guess. The Kohn-Sham energy functional is

$$\mathcal{E}[n(\mathbf{r})] = T_s[n(\mathbf{r})] + \mathcal{E}_{ext}[n(\mathbf{r})] + \mathcal{E}_H[n(\mathbf{r})] + \mathcal{E}_{xc}[n(\mathbf{r})] \quad (31)$$

$T_s[n(\mathbf{r})]$  is the non-interacting kinetic energy functional which we already looked at. We include it as our “best-guess” for the interacting kinetic energy functional since it is exact in the non-interacting problem. Of course the interacting kinetic energy functional isn't identical and we don't know what physics we are missing. But let's not worry about this yet. Let's go over the other terms first.  $\mathcal{E}_{ext}$  is the external energy we have seen many times:

$$\mathcal{E}_{ext}[n(\mathbf{r})] = \int d\mathbf{r} n(\mathbf{r}) v(\mathbf{r})$$

This is true in the interacting and non-interacting problems. We have also seen (in a different form) the  $\mathcal{E}_H$  term before when studying the Hartree and Hartree-Fock approximations. It is the Hartree energy:

$$\mathcal{E}_H[n(\mathbf{r})] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) u(\mathbf{r}, \mathbf{r}') n(\mathbf{r}')$$

If e.g.  $u(\mathbf{r}, \mathbf{r}')$  is the Coulomb interaction, this is our best guess for the Coulomb energy. Note that it includes the same self-interaction errors we saw before. The final term is called the “exchange-correlation” energy. We have crammed everything we don't know into it: it includes all of the interacting kinetic energy we are neglecting, all of the dynamical correlation (e.g. screening), and all exchange interactions. It even includes the corrections that remove self-interaction from the Hartree energy. The Hohenberg-Kohn theorems in §2.4.1 prove that  $\mathcal{E}_{xc}[n(\mathbf{r})]$  exists so this is, in principle, an **exact** reformulation of the many-body problem.

Now let's apply the variational method to solve this energy functional. Minimization with respect to the density is equivalent to minimization with respect to the Kohn-Sham (KS) orbitals [28]

$$\frac{\delta \mathcal{E}}{\delta \psi_{i,\sigma}^*(\mathbf{r})} = \epsilon_{i,\sigma} \psi_{i,\sigma}(\mathbf{r})$$

$\epsilon_{i,\sigma}$  is a Lagrange multiplier included to impose the orthonormality constraint on the KS orbitals. It's not clear how to differentiate the exchange-correlation energy with respect to the KS orbitals, but we can use the “chain rule” for functional derivatives to write

$$\frac{\delta \mathcal{E}_{xc}}{\delta \psi_{i,\sigma}^*(\mathbf{r})} = \frac{\delta \mathcal{E}_{xc}}{\delta n(\mathbf{r})} \frac{\partial n(\mathbf{r})}{\partial \psi_{i,\sigma}^*(\mathbf{r})} = \frac{\delta \mathcal{E}_{xc}}{\delta n(\mathbf{r})} \psi_{i,\sigma}(\mathbf{r})$$

The rest of the functional derivatives with respect to KS orbitals are easy and we find the Kohn-Sham equations:

$$\hat{\mathcal{H}}_{KS} \psi_{i,\sigma}(\mathbf{r}) = \left[ -\frac{\hbar^2}{2m_e} \nabla^2 + v_{KS} \right] \psi_{i,\sigma}(\mathbf{r}) = \epsilon_{i,\sigma} \psi_{i,\sigma}(\mathbf{r}) \quad (32)$$

where we introduced the Kohn-Sham potential

$$v_{KS}(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad (33)$$

$v_{xc}(\mathbf{r})$  is called the exchange-correlation potential and  $v_H(\mathbf{r})$  is the Hartree potential (the same as in eq. 10, but repeated here for concreteness):

$$v_{xc}(\mathbf{r}) = \frac{\delta \mathcal{E}_{xc}}{\delta n(\mathbf{r})}$$

$$v_H(\mathbf{r}) = \int d\mathbf{r}' n(\mathbf{r}') u(\mathbf{r}, \mathbf{r}')$$

The KS equations eq. 32 form a set of auxiliary equations for the basis functions of the density. There is one KS equation for every basis function and each of them looks exactly like a TISE with the Hamiltonian  $\hat{\mathcal{H}}_{KS}$  given in eq. 32. Solving the set of KS equations is equivalent to solving for the density that minimizes the KS energy functional, eq. 31. Note that, just like in the Hartree and Hartree-Fock approximations, this is a SCF problem since the Hartree and exchange-correlation potentials are functionals of the density. The KS equations can easily be formulated as a secular equation just like in §2.2.3 and solved by diagonalization. We will spend a lot of time learning how to solve the KS equations in practice later, so let's not say any more now.

The KS eigenvalues,  $\epsilon_{i,\sigma}$  are not really energies, but they are usually called energies. The KS orbitals formally have limited physical meaning. They are auxiliary functions, but they are often interpreted as physical electron wave-functions **this needs a lot of follow up discussion**. The KS energies are related to the ground-state energy through the KS energy functional (see exercise 5.4 in ref. [71]):

$$\mathcal{E}[n(\mathbf{r})] = \sum_{i,\sigma} f_{i,\sigma} \epsilon_{i,\sigma} - \mathcal{E}_H[n(\mathbf{r})] - \int d\mathbf{r} n(\mathbf{r}) v_{xc}(\mathbf{r}) + \mathcal{E}_{xc}[n(\mathbf{r})] \quad (34)$$

It turns out that there is some subtlety in including partial occupations  $f_{i,\sigma}$  in the KS scheme. e.g. if arbitrary variations in  $f_{i,\sigma}$  are allowed, the energy functional is not variational [35]. Or if the Fermi-Dirac function is used and we wish to interpret the results at finite temperature, we have to minimize the *free-energy* instead of the energy [42]. But let's not worry about these issues now. Just assume we are minimizing at fixed occupation numbers which are determined by the self-consistency conditions on the density.

### 2.4.3 Orbital Energies

**Should include discussion of how to interpret energies in DFT. Ref. [71] has nice discussion of this. Even talks about COHSEX, RPA, etc. for understanding excited states.**

### 2.4.4 The Stupidity Energy

So far we have made no approximations; we have only re-arranged the ground-state energy functional into a different form. In principle, this is an exact method. In practice, we don't know what  $\mathcal{E}_{xc}[n(\mathbf{r})]$  is. Richard Feynman called it the “stupidity energy” because it

contains everything we don't know and we don't know what it is. It usually just called the exchange-correlation (XC) energy. Still, a *lot* of effort has been devoted to coming up with approximations to the XC energy. **We will look at them in detail later. For now, let's be vague.**

Typically the XC energy is approximated by fitting a parameterization to exact (numerical) results for the interacting homogeneous electron gas. There is a hierarchy of approximations of increasing complexity. Roughly speaking, the exchange-correlation potential (or energy) is Taylor expanded in moments of the density:

$$v_{xc}[n(\mathbf{r})] = v_{xc}[n(\mathbf{r}_0), \nabla n(\mathbf{r}_0), \nabla^2 n(\mathbf{r}_0), \dots]$$

Keeping only the lowest order term is the local density approximation (LDA). The exchange-correlation energy in the LDA is written

$$\mathcal{E}_{xc}^{LDA}[n(\mathbf{r})] = \int d\mathbf{r} \epsilon_{xc}[n(\mathbf{r})]n(\mathbf{r})$$

where  $\epsilon_{xc}[n(\mathbf{r})]$  is the exchange-correlation energy per particle of the homogeneous electron gas evaluated at the density  $n(\mathbf{r})$ . Parameterizations that keep the next moment of the density, its gradient  $\nabla n(\mathbf{r})$ , are called generalized gradient approximations (GGAs). Approximations keeping the next order term,  $\nabla^2 n(\mathbf{r})$ , are called meta-generalized gradient approximations (meta-GGAs). There are many different types of LDAs, GGAs, and even meta-GGAs. They are available in most codes through the exchange-correlation library LIBXC. For the most part, these are “plug-and-play” in modern DFT: you calculate a density, hand it off to LIBXC, and it returns the exchange-correlation potential and energy.

It's also worth mentioning hybrid functionals. The Hartree potential in the KS equations results in so called “self-interaction” errors. These errors have important consequence in many cases **give examples**. In the Hartree-Fock approximation, we saw that the exchange interaction canceled the self interaction in the Hartree potential. This fact suggests the following method: the exact exchange energy is calculated from the exchange operator in eq. 24 using the KS orbitals. The exchange contribution to the exchange-correlation energy is removed and replaced by the exact exchange. The results are sometimes excellent and sometimes awful. In any case, exact exchange is very expensive to calculate. An exchange-correlation functional that includes exact exchange is called a “hybrid functional.”

## 2.5 Remarks

To convince ourselves why all this was worth discussing and to get a feel for what we will use it all for later, let's make a few observations. The external potential in eq. 34 will almost always be the Coulomb field of atomic nuclei. Let's treat the nuclei as classical point-particles at zero temperature (so that the kinetic energy vanishes). The total energy of the crystal system

$$\mathcal{E}_{tot}(\mathbf{R}) = \mathcal{E}_{KS}(\mathbf{R}) + \frac{k}{2} \sum_{I \neq J} \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (35)$$

$\mathcal{E}_{KS}(\mathbf{R})$  is the KS total energy in eq. 34, here written explicitly as a function of the nuclear coordinates. The other term is the nuclear-nuclear Coulomb interaction. Minimizing

the total energy with respect to  $\mathbf{R}$  determines the equilibrium atomic structure of matter. Comparison to experimental data using X-ray or neutron scattering has shown that DFT is an extraordinarily accurate method. Derivatives of eq. 35 give us the forces on the nuclei. We can use the forces to perform ab-initio molecular dynamics simulations. If the forces are taken around equilibrium, we can calculate the phonon spectra. Comparing the phonon spectra to inelastic neutron scattering measurements has also confirmed the extraordinary success of DFT. Beyond simple comparison to experiment, DFT also allows exploring new phases of matter. For instance, it is usually very difficult to study matter under extreme pressure in the laboratory. However, high pressure phases of matter can readily be studied in DFT by “relaxing” the atomic coordinates under pressure.

It is also important to note that so far, we haven’t assumed anything about the structure of the matter we are studying. In normal condensed matter settings, DFT has been applied to study isolated atoms and molecules, gases and liquids, ordered and disordered solids, and even plasmas. Furthermore, we haven’t even assumed anything about the interactions. They could be Coulomb interactions between charged particles, but could also be more exotic interactions e.g. the phonon-mediated attractive interaction between Cooper pairs. In fact there exists a density functional formulation of the superconducting state called “superconducting density functional theory.” Other types of density functional theory are...

The derivative of Coulomb can be calculate by Ewald method [44].

### 3 Crystals

From refs. [69, 87] and §2.1.3 in Martin [51]. Most solids that are easy to study are *crystalline*. This means that they possess a discrete translation symmetry classified by the crystalline lattice. The lattice is a set of points generated by integral combinations of the lattice vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$ . A generic point in the lattice is given by

$$\mathbf{R}_{\{n_1, n_2, n_3\}} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

Notes on notation: once the lattice vectors are given in a particular setting, it is reasonably to specify a point in the crystal simply by the set of numbers  $\mathbf{n} \equiv \{n_1, n_2, n_3\}$ . Often one simply writes  $\mathbf{R}_\mathbf{n}$  or just  $\mathbf{R}_n$ .

It is also possible to associate a *basis* with each point in the lattice. The basis is the fundamental “unit” of atoms that make up the crystal. The “cell” containing the basis is usually called the “unitcell”. To be more precise, the unitcell is the volume of space contained between planes placed perpendicular to the lattice vectors and half-way between the lattice points. The boundaries of the unitcell are the lines formed by the intersections of the planes. Such a volume is called a *Wigner-Seitz* cell. In many elemental crystals, like face-centered-cubic Ag, there is only one atom per unitcell. This is very uncommon however. Most interesting crystals nowadays have many atoms per unit-cell. e.g.  $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$  has 54 atoms per unitcell. The positions of the atoms are usually specified relative to the origin of the unitcell the atom is in. For instance, suppose we want to know the absolute coordinate of the  $i^{\text{th}}$  atom in unitcell  $\mathbf{n}$ . Call  $\boldsymbol{\tau}_i$  the atom’s position relative to the unitcell’s origin.  $\boldsymbol{\tau}$  is the same in every unitcell. The absolute position of the atom is then  $\mathbf{r}_{n,i} \equiv \mathbf{R}_\mathbf{n} + \boldsymbol{\tau}_i$ . If there are multiple atoms in the basis, then we have to specify the set of coordinates  $\{\boldsymbol{\tau}\}$ .

The choice of lattice vectors isn’t unique. There are many different ways to pick them that generate an equivalent crystal. A crystal is technically classified by its space group: this is the group theoretic name for the set of symmetry operations on a lattice and its basis that leave the crystal invariant. For a given space group, there exists a minimal volume Wigner-Seitz cell called the *primitive* unitcell. But we don’t have to pick the smallest one. For example, sometimes it is convenient to use a different set of lattice vectors that are orthogonal to one-another. This makes some parts of a calculation simpler at the cost of a larger unitcell that contains more atoms. A unitcell that is not primitive is called a *conventional* unitcell.

It turns out that doing physics in crystals offers some neat advantages. In physics we are used to using symmetries to make a problem easier. This is true in solid state physics too. For a crystal Hamiltonian of the form

$$\hat{H}(\mathbf{r}) = \frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r})$$

we expect it to be true that  $V(\mathbf{r} + \mathbf{R}) \equiv V(\mathbf{r})$ .  $\mathbf{R}$  is an arbitrary lattice vector. This is because each unitcell is identical (i.e. there is periodicity, see fig. 1). Then it is true that  $\hat{H}(\mathbf{r} + \mathbf{R}) = \hat{H}(\mathbf{r})$ . We say the Hamiltonian has “discrete translation symmetry”. As we will now see, the discrete translational symmetry of the lattice allows us to invoke “Bloch’s theorem,” which greatly simplifies solving the Schrödinger’s equation in solids.<sup>7</sup>

<sup>7</sup> Group theory can also be applied to solid state physics problems in many much more technical ways; e.g.

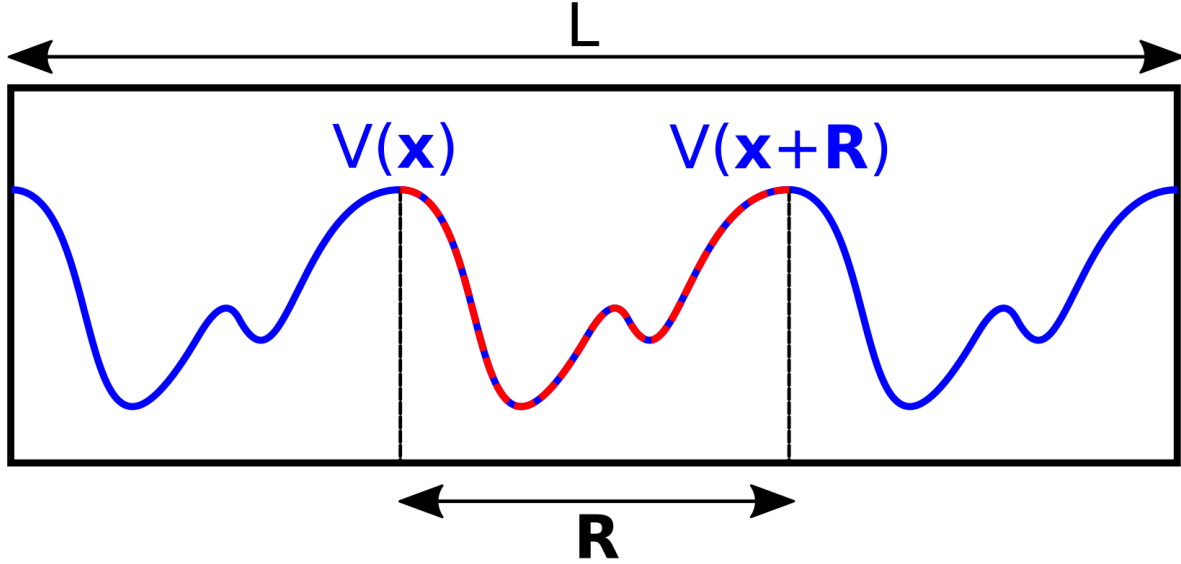


Fig. 1: A periodic potential  $V(\mathbf{x})$  with periodicity  $\mathbf{R}$  in a box of length  $L$ .

### 3.1 Bloch's Theorem

See §4.3 in Sakurai [64], Chp. 1 in Ziman [87], or practically any other book on solid state physics. Bloch's theorem is just a rather general statement about the form of eigenstates of a Hamiltonian in a periodic potential, e.g. in solids. Let's see what Bloch's theorem says.

Assume we are dealing with a Hamiltonian of the form  $\hat{\mathcal{H}}(\mathbf{x}) = \hat{\mathbf{p}}^2/2m + V(\mathbf{x})$  where the potential  $V(\mathbf{x}) = V(\mathbf{x} + \mathbf{R})$  is periodic under translation by a lattice vector  $\mathbf{R}$ . Define the *translation* operator  $\hat{T}_{\mathbf{R}}$  that formally changes the coordinates  $\mathbf{x} \rightarrow \mathbf{x} + \mathbf{R}$ . It's action on the Hamiltonian is:  $\hat{T}_{\mathbf{R}}^\dagger \hat{\mathcal{H}}(\mathbf{x}) \hat{T}_{\mathbf{R}} = \hat{\mathcal{H}}(\mathbf{x})$  which follows from the periodicity of the potential. Clearly it's a unitary operator and its commutation relation with the Hamiltonian is

$$[\hat{T}_{\mathbf{R}}, \hat{\mathcal{H}}(\mathbf{x})] = 0$$

The translation operator commutes with the Hamiltonian, so eigenstates of the translation operator are eigenstates of the Hamiltonian! What are the eigenstates of the translation operator?

Let  $\psi(\mathbf{x})$  be an eigenstate of the translation operator. Since  $\hat{T}_{\mathbf{R}}$  is unitary, it's eigenvalues can only be a phase. Specialize to translation by only a single basis vector:

$$\hat{T}_{\mathbf{a}_1} \psi(\mathbf{x}) = \exp(i\theta_1) \psi(\mathbf{x})$$

$\theta_1$  is a real number. Then translation by an arbitrary lattice vector  $\mathbf{R} \equiv n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$  has to give

$$\hat{T}_{\mathbf{R}} \psi(\mathbf{x}) = \exp(i(n_1 \theta_1 + n_2 \theta_2 + n_3 \theta_3)) \psi(\mathbf{x}) \equiv \exp(i\mathbf{k} \cdot \mathbf{R}) \psi(\mathbf{x})$$

---

we can use our knowledge of the space group of a crystal to “block-diagonalize” its Hamiltonian. This reduces the problem of diagonalizing a large Hamiltonian into diagonalizing a set of smaller subspace Hamiltonians. This stuff is very cool, but very abstract. See the amazing book by the amazing Mildred Dresselhaus [22]



where the sum was parameterized by the *definition*  $\mathbf{k} \cdot \mathbf{a}_i = \theta_i$ . So we can label solutions of the periodic Hamiltonian by a vector  $\mathbf{k}$ . Finally, define the following function:

$$u_{\mathbf{k}}(\mathbf{x}) = \exp(-i\mathbf{k} \cdot \mathbf{x})\psi_{\mathbf{k}}(\mathbf{x})$$

This is a periodic function as can be seen by

$$\begin{aligned} u_{\mathbf{k}}(\mathbf{x} + \mathbf{R}) &= \exp(-i\mathbf{k} \cdot (\mathbf{x} + \mathbf{R}))\psi_{\mathbf{k}}(\mathbf{x} + \mathbf{R}) \\ &= \exp(-i\mathbf{k} \cdot \mathbf{x}) \exp(i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}))\psi_{\mathbf{k}}(\mathbf{x}) \\ &= \exp(-i\mathbf{k} \cdot \mathbf{x})\psi_{\mathbf{k}}(\mathbf{x}) \equiv u_{\mathbf{k}}(\mathbf{x}) \end{aligned}$$

The statement of Bloch's theorem is that the solutions of the Schrödinger's equation with a periodic potential can be represented by a plane-wave times a unitcell-periodic function

$$\boxed{\psi_{\mathbf{k}}(\mathbf{x}) = \exp(i\mathbf{k} \cdot \mathbf{x})u_{\mathbf{k}}(\mathbf{x})} \quad (36)$$

as we have just verified.

### 3.2 Plane Waves

Above, we introduced the vector  $\mathbf{k}$  when deriving Bloch's theorem. What is this vector? In mechanics, Noether's theorem tells us that a system with continuous translational symmetry conserves momentum. This is almost true for crystals: we have discrete translational symmetry, so *crystal momentum* is conserved. The vector  $\mathbf{k}$  is crystal momentum.

Let's recall some stuff about the solutions of a Hamiltonian with continuous symmetry: the simplest conceivable such Hamiltonian is the free-particle  $\hat{\mathcal{H}} = \hat{p}^2/(2m) = -\hbar^2\nabla^2/(2m)$ . Momentum is conserved so the solutions are momentum eigenstates  $|\mathbf{k}\rangle$ . In position representation,  $\langle \mathbf{x}|\mathbf{k}\rangle = c \exp(i\mathbf{k} \cdot \mathbf{x})$ . The normalization factor,  $c$ , needs to be determined. There is an issue, however. If we put the system in infinite space and try to normalize in the usual way

$$1 = \langle \mathbf{k}|\mathbf{k}\rangle = \int d\mathbf{x} \langle \mathbf{k}|\mathbf{x}\rangle \langle \mathbf{x}|\mathbf{k}\rangle = |c|^2 \int d\mathbf{x} = \infty$$

we find that it is impossible. The way around this issue is to put the system into a finite "box" of volume  $V \equiv L^3$ . Then it is found that  $c = V^{-1/2} \equiv L^{-3/2}$ . Momentum eigenstates are often called "plane-waves" and their quantum number is their momentum,  $\mathbf{k}$ . Explicitly, momentum eigenstates are

$$\psi_{\mathbf{k}}(\mathbf{x}) = \frac{1}{V^{1/2}} \exp(i\mathbf{k} \cdot \mathbf{x}) \quad (37)$$

The wave-functions in eq. 37 are the solutions of the free-particle Hamiltonian. There is still an issue, however. Recall that the free-particle TISE is a  $2^{nd}$  order differential equation, thus requiring two boundary conditions. One is taken care of by normalization. The other is given by the wave-function's value on the box boundaries. For example, in the infinite well problem, we demand the wave-function is 0 at the boundaries. In solid state physics, however, a more convenient choice is *periodic boundary conditions*.

### 3.2.1 Periodic Boundary Conditions; Crystal Momentum

The solutions of the Schrödinger's equation with a periodic Hamiltonian satisfy Bloch's theorem (we call them “Bloch functions”). Bloch's theorem says the (un-normalized) solutions are

$$\begin{aligned}\psi_{n\mathbf{k}}(\mathbf{r}) &= \exp(i\mathbf{k} \cdot \mathbf{r})u_{n\mathbf{k}}(\mathbf{r}) \\ u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) &= u_{n\mathbf{k}}(\mathbf{r})\end{aligned}$$

where  $n$  is the “band index” (there are  $N_b$  of them with  $N_b$  labeling the number of variational basis orbitals) and  $\mathbf{k}$  is a quantum number of the system. It is called *crystal* momentum and is almost conserved like usual momentum: unlike momentum, crystal momentum is only conserved modulo a reciprocal lattice vector. Let us see what this means.

The system is placed into a “box” of volume  $V$  and periodic boundary conditions (PBC) are imposed. There are  $N = N_1 N_2 N_3$  unitcells with  $N_i$  labeling the number of unitcells along the  $i^{th}$  direction. Then from the requirement  $\psi_{n\mathbf{k}}(\mathbf{R}_N) = \psi_{n\mathbf{k}}(\mathbf{R}_0)$ , with  $\mathbf{R}_N$  a vector connecting a point on the opposite side of the box that must satisfy PBC with the point  $\mathbf{R}_0$ , we find

$$\begin{aligned}\exp(i\mathbf{k} \cdot \mathbf{R}_N)u_{n\mathbf{k}}(\mathbf{R}_N) &= \exp(i\mathbf{k} \cdot \mathbf{R}_0)u_{n\mathbf{k}}(\mathbf{R}_0) = \\ \exp(i\mathbf{k} \cdot \mathbf{R}_N) &= \exp(i\mathbf{k} \cdot \mathbf{R}_0)\end{aligned}$$

where we used periodicity of the functions  $u_{n\mathbf{k}}(\mathbf{r})$ . This equation must hold for all points on the edges of the box that are connected by a lattice vector, so let us just pick  $\mathbf{R}_0 \equiv 0$  to be the origin for convenience. We find that

$$\exp(i\mathbf{k} \cdot \mathbf{R}_N) = 1$$

which requires

$$\begin{aligned}\mathbf{k} \cdot \mathbf{R}_N &= 2\pi(N_1 n_1 + N_2 n_2 + N_3 n_3) = 2\pi n \\ n &\in \mathbb{Z}\end{aligned}$$

We chose to write  $\mathbf{k} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3$  in a basis such that  $\mathbf{a}_i \cdot \mathbf{b}_j \equiv 2\pi \delta_{ij}$ . The  $\mathbf{b}_i$  chosen this way are called reciprocal lattice vectors. They are

$$\mathbf{b}_i = \epsilon_{ijk} \frac{2\pi}{\Omega} \mathbf{a}_j \times \mathbf{a}_k \quad (38)$$

$\Omega$  is the volume of the primitive unitcell. Then  $n_i \equiv m_i/N_i$  and  $k_i = 2\pi m_i/N_i$  with  $m_i \in \mathbb{Z}$ . Evidently we don't need to consider wave-vectors  $k_i$  with  $m_i \equiv (m'_i + N_i) > N_i$  since  $\exp(i2\pi(m'_i + N_i)/N_i) = \exp(i2\pi m'_i/N_i)$  with  $m'_i \leq N_i$ .

Restricting  $m_i \leq N_i$  means that  $k_i \leq b_i$ . The region of reciprocal space spanned by  $\mathbf{b}_i$  is called the *first Brillouin zone* (1BZ).  $\mathbf{k}$  are wave-vectors that lie on a uniform grid in the 1BZ and there are  $N = N_1 N_2 N_3$  of them. A  $\mathbf{k}'$  that lies outside the 1BZ is equivalent to all points connected to it by a reciprocal lattice vector, including  $\mathbf{k}$  in the 1BZ, so that we only need to study wave-vectors that lie in the 1BZ. This is the essence of crystal momentum. The importance of Bloch's theorem is that we only have to solve the Schrödinger's equation for the finite number  $N$  wave vectors  $\mathbf{k}$  that lie in the 1BZ.

Usually instead of restricting  $m_i \leq N_i$ , we pick  $-N_i/2 < m_i \leq N_i/2$ . In “reciprocal lattice units,” we specify the wave-vector in units where  $n_i = m_i/N_i$  so that we have  $-1/2 < n_i \leq 1/2$  which is convenient notation because it is independent of the system size.

Let us also work out the normalization of the Bloch functions. Supposing that  $\psi_{n\mathbf{k}}(\mathbf{r}) = c_{n\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) u_{n\mathbf{k}}(\mathbf{r})$  we demand that

$$\begin{aligned} \langle \psi_{n\mathbf{k}} | \psi_{n\mathbf{k}} \rangle &= |c_{n\mathbf{k}}|^2 \int d\mathbf{r} |u_{n\mathbf{k}}(\mathbf{r})|^2 \\ &= N |c_{n\mathbf{k}}|^2 \int_{\Omega} d\mathbf{r} |u_{n\mathbf{k}}(\mathbf{r})|^2 = 1 \end{aligned}$$

The second line follows from periodicity. Integrating over “ $\Omega$ ” means to only integrate over a single unitcell located at the origin. If we resolve to normalize the unitcell periodic part of the Bloch functions,  $u_{n\mathbf{k}}(\mathbf{r})$ , such that  $\langle u_{n\mathbf{k}} | u_{n\mathbf{k}} \rangle \equiv \int_{\Omega} d\mathbf{r} |u_{n\mathbf{k}}(\mathbf{r})|^2 = 1$ , then  $c_{n\mathbf{k}} = N^{-1/2}$ .

Another reason to impose PBCs is that we can systematically take the limit of an infinite volume box with all volume-dependent factors cancelling. In solid state physics, this means we can model an infinite crystal without ever having to care about what happens at its surface. With that in mind, we mention that is very common to encounter sums of the form

$$V^{-1} \sum_{\mathbf{k}}$$

where the sum runs over all points in the 1BZ. This can be inconvenient to work with analytically; numerically, evaluating sums is straightforward... anyway, this is where taking the infinite volume limit comes in handy. Recall that  $\mathbf{k}$  is a discrete set spaced  $2\pi n/L$  apart. 2 points spaced a single integer apart have spacing  $\Delta n$ . Then  $\Delta k = 2\pi \Delta n/L$ . In the limit  $L \rightarrow \infty$ ,  $\Delta k$  becomes infinitesimal. Then  $dn = L \cdot dk/(2\pi)$ . Thus, we arrive at the “rule” for taking the infinite volume limit

$$V^{-1} \sum_{\mathbf{k}} \rightarrow \int \frac{d\mathbf{k}}{(2\pi)^3} \quad (39)$$

The rule in eq. 39 comes up very often in calculations.

### 3.3 Fourier Transforms

As we have seen, we repeatedly try to generalize from the free-particle, which has continuous symmetry, to a crystal, which has discrete translational symmetry. What’s the difference? The kinetic energy is manifestly translationally invariant, so the difference is in the potential. Ignoring interactions between electrons (interactions can spontaneously break symmetry), the potential is the electrostatic interaction between an electron and the nuclei. But we already said that in a crystal, the nuclei form an ordered arrangement. This means that if we (or the crystal) move by an arbitrary number of lattice vectors, the potential is identical. i.e.

$$V(\mathbf{x}) = V(\mathbf{x} + \mathbf{R})$$

A diagram of  $V(\mathbf{x})$  was shown in fig. 1. Since the potential is periodic, it will be useful to express it (and many other quantities) in Fourier space. Let’s do that now.

Instead of specializing to a potential, we might as well study the Fourier transform of *any* continuous periodic function with periodicity  $\mathbf{R}$  in a box with size  $V = L^3$ . Call the function  $f(\mathbf{x})$ . It is expressible as a sum of plane-waves, eq. 37

$$f(\mathbf{x}) = \sum_{\mathbf{G}} f_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{x}) \quad (40)$$

Because  $f(\mathbf{r})$  has the periodicity of the lattice, we only need to consider wave-vectors that belong to the reciprocal lattice. Let  $\mathbf{b}_i$  be the primitive reciprocal lattice vectors. Then  $\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$  is a general reciprocal lattice vector. Let's check that these are the only components that contribute to  $f(\mathbf{x})$ . Consider a wave-vector  $\mathbf{Q} = \mathbf{q} + \mathbf{G}$  with  $\mathbf{q}$  some wave vector other than a reciprocal lattice vector. Then translation by a lattice vector  $\mathbf{R}$  results in  $\exp(i\mathbf{Q} \cdot (\mathbf{x} + \mathbf{R})) = \exp(i\mathbf{Q} \cdot \mathbf{x}) \exp(i\mathbf{q} \cdot \mathbf{R}) \neq \exp(i\mathbf{Q} \cdot \mathbf{x})$  which is not periodic and thus it's Fourier coefficient must be identically 0. Note that in the special case  $f(\mathbf{x})$  is real

$$f(\mathbf{x}) \equiv f^*(\mathbf{x}) = \sum_{\mathbf{G}} f_{\mathbf{G}}^* \exp(-i\mathbf{G} \cdot \mathbf{x}) = \sum_{\mathbf{G}} f_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{x})$$

implies that  $f_{\mathbf{G}}^* = f_{-\mathbf{G}}$ . This can be used to reduce the number of Fourier coefficients that have to be explicitly calculated.

The *non-zero* Fourier coefficients in eq. 40 are determined using orthogonality.

$$\begin{aligned} \int d\mathbf{x} f(\mathbf{x}) \exp(-i\mathbf{G}' \cdot \mathbf{x}) &= \sum_{\mathbf{G}} \int d\mathbf{x} f_{\mathbf{G}} \exp(i(\mathbf{G} - \mathbf{G}') \cdot \mathbf{x}) \\ &= V \sum_{\mathbf{G}} f_{\mathbf{G}} \delta_{\mathbf{G}, \mathbf{G}'} \end{aligned}$$

Then we have

$$\begin{aligned} f_{\mathbf{G}} &= V^{-1} \int d\mathbf{x} f(\mathbf{x}) \exp(-i\mathbf{G} \cdot \mathbf{x}) \\ &= \Omega^{-1} \int_{\Omega} d\mathbf{x} f(\mathbf{x}) \exp(-i\mathbf{G} \cdot \mathbf{x}) \end{aligned} \quad (41)$$

where, in the last line, periodicity of  $f(\mathbf{x})$  was used to reduce the integral down to a single unitcell centered at the origin.

## 4 Lattice Dynamics

See [80] for a cut-and-dry derivation of lattice dynamical equations and, even better, a derivation of the scattering function! This will loosely follow Dove [21], Ziman [87], and Ashcroft and Mermin [6] but is mostly just free-styling.

We want to study the dynamics of the atoms in matter. Start off by assuming that the nuclei are classical, then solve for the equations of motion. The forces on the particles can be calculated from eq. 35

$$U(\mathbf{r}) = \mathcal{E}_{BO}(\mathbf{r}) + \frac{k}{2} \sum_{I \neq J} \frac{e^2 Z_I Z_J}{|\mathbf{r}_I - \mathbf{r}_J|}$$

The force on a given atom is  $\mathbf{f}_i = \partial U / \partial \mathbf{r}_i$ . Here,  $\mathbf{r}_i$  are coordinates of nuclei, not electrons. We won't need to write down the electron coordinates again for a while. This equation was derived in the adiabatic approximation so  $\mathcal{E}_{BO}$  is the Born-Oppenheimer electronic energy surface. It can be calculated in the Hartee-Fock approximation, in DFT from the Kohn-Sham equations (eq. 34), or other ways. The other term is just the mutual Coulomb repulsion between the nuclei. The electrons *screen* the nuclei so that their interaction isn't purely electrostatic. The screening is contained in  $\mathcal{E}_{BO}$ . In principle, this equation contains everything we need to calculate the classical trajectories of the nuclei.

The derivative of the Coulomb energy is easy. The expensive part is calculating  $\partial \mathcal{E}_{BO} / \partial \mathbf{r}_i$ . We already saw how to do it in ... From now on, let's assume that we always know how to calculate derivatives of the  $\mathcal{E}_{BO}$  and just focus on solving the resulting equations.

That's all neat, but nobody knows how to solve Newton's equations analytically for more than 2 particles. Still, it's easy to do using numerical integration, e.g. the *Verlet* method. Using the Kohn-Sham energy is called ab-initio molecular dynamics (AIMD). Using a tight-binding approximation for  $\mathcal{E}_{BO}$  is still considered "quantum" and is called tight-binding molecular dynamics (TBMD). Using an empirical approximation to  $\mathcal{E}_{BO}$  is called classical molecular dynamics (MD). Solving the classical Newton equations once the forces are known is actually very cheap computationally. Let's just focus on AIMD for now. Calculating the forces from the Kohn-Sham energy requires solving the Kohn-Sham equations and is very expensive, meaning AIMD is very expensive.

### 4.1 Phonons

*copy from phonons notes*

## 5 Polarization

The technical details on the *modern theory* section will follow Vanderbilt's book [75] and, for the phonons part, Resta's notes on topology in band theory [62]. But first, we will warm up on the simple models for polarization. Some terminology:

- *linear dielectrics*: linear dielectrics are defined by their response to external electric fields. Specifically, the induced polarization is proportional to the external field:  $\mathbf{P} = \alpha \mathbf{E}$ . In this equation,  $\alpha$  is a scalar function, so that the material is isotropic. In anisotropic dielectrics (practically all of them), the coefficient  $\hat{\alpha}$  is a  $3 \times 3$  tensor. This equation is the lowest order term in a Taylor expansion and is often valid if  $\mathbf{P}(\mathbf{E} = 0) = 0$ .
- *paraelectric*: these have *non-linear* response to external fields.
- *ferroelectrics*: these have  $\mathbf{P}(\mathbf{E} = 0) \neq 0$ , i.e. they have non-zero polarization even in the absence of an external field.

Let's party.

### 5.1 Simple Model

Let's use Tong's notes [73] (and maybe Jackson [40]).

For now, we will only focus on insulators (i.e. no free charge). This is because, in conductors (which do have free charge), the charge always reorients to cancel the external field. In the context of electromagnetism (EM), insulators are just called dielectrics.

In our simple model, we assume matter is made up of neutral atoms. The atoms possess a positively charged core and a negatively charged electron distribution that is tightly bound to the core. For a weak enough field (i.e. not strong enough to ionize the atoms), the positive charged nuclei and the dense electron cloud separate slightly: the neutral atoms polarize to form dipoles. See fig. 2. Recall from electrostatics that the electric field for a point charge is

$$\phi(\mathbf{x}) = k_C \frac{q}{|\mathbf{x}|}$$

$k_C$  is the "Coulomb constant". We take the vector separating the nuclei and electron cloud to be  $\mathbf{d}$ . The separation distance is  $d$ . Using linearity, we can write the potential for the dipole as

$$\phi(\mathbf{x}) = qk_C \left( \frac{q}{|\mathbf{x}|} - \frac{q}{|\mathbf{x} + \mathbf{d}|} \right)$$

Assume we are looking sufficiently far from the dipole so that  $d \ll x$ . This is usually *very* sensible in matter. Then we can approximate

$$\frac{1}{\sqrt{(\mathbf{x} + \mathbf{d})^2}} \approx \frac{1}{|\mathbf{x}|} - \frac{\mathbf{d} \cdot \mathbf{x}}{|\mathbf{x}|^3} + O(d^2)$$

and write the potential as

$$\phi(\mathbf{x}) = k_C \frac{\mathbf{p} \cdot \mathbf{x}}{|\mathbf{x}|^3} \quad (42)$$

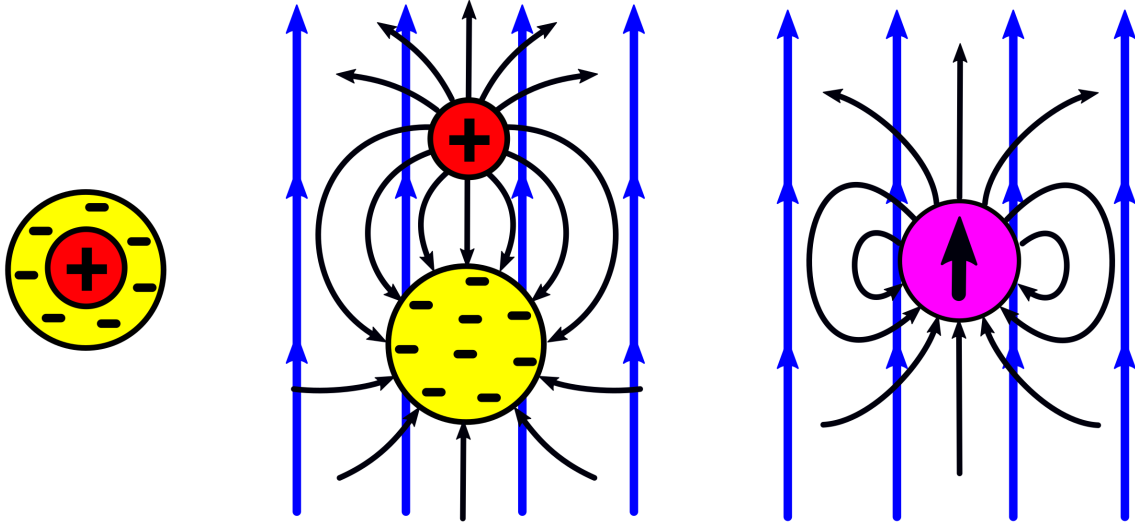


Fig. 2: (Left) a neutral atom. The red circle is a positively charged nuclei, the yellow circle is the electron clouds. (Center) An applied electric field (blue) polarizes the neutral atom. The dipole field due to displaced charges is in black. (Right) A point dipole

where we introduced the *dipole moment*:  $\mathbf{p} = q\mathbf{d}$ . This is exact for a *point dipole*: i.e.  $d \rightarrow 0$  while  $qd$  remains finite. The field is, as usual,  $\mathbf{E} = -\nabla\phi(\mathbf{x})$ .

For an isolated dipole, the field is a funny looking thing. But in a crystal, the funny looking parts cancel so that the net result, at least in the case of a constant field, is a constant polarization field. This is shown in fig. 3. In many materials, it is true that the induced polarization is proportional to the applied field:  $\mathbf{p} = \alpha\mathbf{E}$ . We call these materials *linear dielectrics*.

As an example, let's step back and consider the isolated atom. Take the nucleus to be an infinitely localized point charge sitting at the center of a uniform charged sphere, i.e. the electronic density. Let the sphere have radius  $a$ . The field inside a uniform sphere is

$$\mathbf{E} = k_C \frac{q}{a^3} \mathbf{x}$$

The polarized atom is at equilibrium when the force due to the external field equals the force due to the electron-nucleus interaction:  $\mathbf{F}_{ext.} = -\mathbf{F}_{E-N}$ . Solving for the separation

$$\mathbf{d} = \frac{a^3}{k_C q} \mathbf{E}$$

gives  $\alpha = a^3/k_C$  which is apparently pretty close to experimental values.

In matter, it makes more sense to talk about intensive quantities. Then we take the polarization to actually be the polarization per unit volume. With  $n$  the number of atoms per unit volume, we have  $\mathbf{P} = n\mathbf{p}$  for the polarization.

... As a final note, it is important to realize that approximating the induced field as a dipole field is really the lowest order in a multi-pole expansion for the field due to the induced charge distribution. It arose naturally from our treatment because we assumed the charges

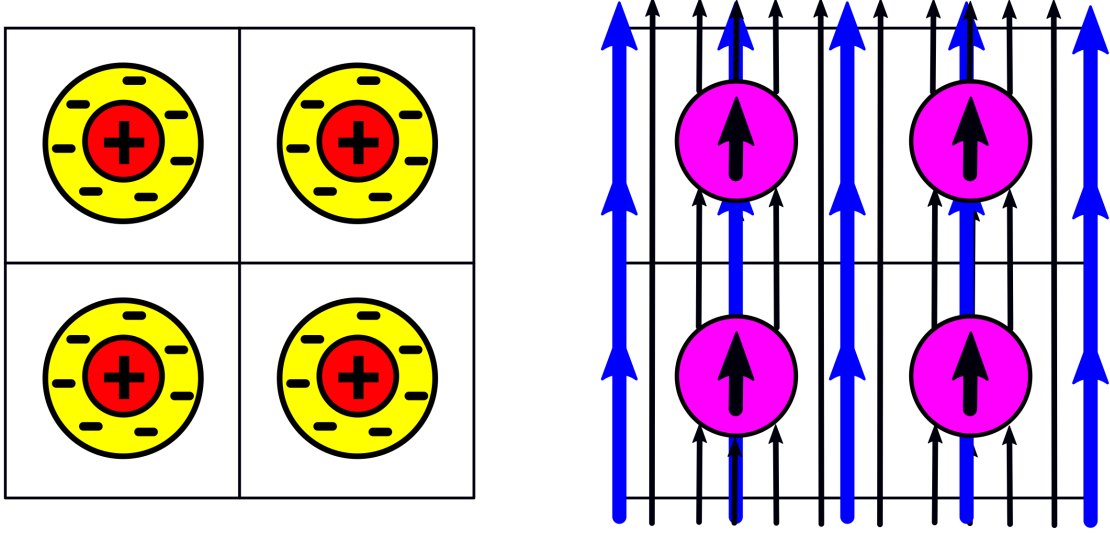


Fig. 3: (Left) a neutral, unpolarized, monatomic crystal. (Right) The response of the crystal to a constant external field.

are rigid balls. In real materials, the charge density around the nucleus changes shape and higher order multi-poles are important too.

### 5.1.1 Bound Charge and Electric Displacement

In a material that is polarized, there is (by necessity), regions of non-zero net charged. E.g. in the case of the polarized atom in fig. 2, the separation of the positive and negative charge results in positively and negatively charged regions. Let's look at this more carefully. The potential from one dipole is given above in eq. 42. Then the potential, integrated over the whole crystal, is

$$\phi(\mathbf{x}) = k_C \int_V \frac{\mathbf{P}(\mathbf{x}') \cdot (\mathbf{x} - \mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|^3} d\mathbf{x}' = k_C \int_V d\mathbf{x}' \mathbf{P}(\mathbf{x}') \cdot \nabla' \left( \frac{1}{|\mathbf{x} - \mathbf{x}'|} \right) d\mathbf{x}'$$

We can integrate this by parts using various identities to find

$$\phi(\mathbf{x}) = k_C \left( \int_{\partial V} \frac{\mathbf{P}(\mathbf{x}') \cdot \hat{\mathbf{n}}'}{|\mathbf{x} - \mathbf{x}'|} dA' - \int_V \frac{\nabla' \cdot \mathbf{P}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}' \right)$$

Each of these terms has a natural interpretation. The first one looks like the potential due to a surface charge distribution  $\sigma_{\text{bound}} = \mathbf{P} \cdot \hat{\mathbf{n}}$ . The other looks like the potential due to a bulk charge distribution  $\rho_{\text{bound}} = -\nabla \cdot \mathbf{P}$ .

As another example, consider the case in fig. 3. Here, the polarization is constant and, averaged over many unit cells, there should be no net charge in the bulk. Indeed,  $\nabla \cdot \mathbf{P} \equiv 0$  for a constant polarization field. In this case, all of the bound charge is on the surface.

It makes sense to conceptually separate the *free* charge and the *bound* charge (this is what other authors call them; in my mind, it makes more sense to call them *external* and



*induced* charges... but I am a moron). Anyway, Gauss's law tells us that the electric field, regardless of whether we are looking in vacuum or matter, is

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0}$$

In terms of the polarization (regardless of whether or not it is linear) we write this as

$$\nabla \cdot \mathbf{E} = \frac{1}{\epsilon_0}(\rho_{\text{ext}} + \rho_{\text{ind}}) = \frac{1}{\epsilon_0}(\rho_{\text{ext}} - \nabla \cdot \mathbf{P})$$

Let us define the *electric displacement* as

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$$

The electric displacement is convenient because it obeys

$$\nabla \cdot \mathbf{D} = \frac{\rho_{\text{ext}}}{\epsilon_0}$$

so that, any material-specific behaviour is including in the definition of the electric displacement itself.  $\mathbf{D}$  satisfies Gauss's law in terms of only the external (i.e. free) charge. For *linear* dielectrics,  $\mathbf{P} \equiv \alpha \mathbf{E}$ . It is common to let  $\alpha \equiv \epsilon_0 \chi_e$  with  $\chi_e$  the *electric susceptibility*. It is always positive. Then

$$\mathbf{D} = \epsilon_0(1 + \chi_e) \mathbf{E} \equiv \epsilon \mathbf{E} \quad (43)$$

$\epsilon \equiv \epsilon_0(1 + \chi_e)$  is the *permittivity*. Since  $\chi_e > 0$ ,  $\epsilon > \epsilon_0$  and, in matter, the electric field is always smaller than in vacuum. In other words, the *dielectric constant*  $\epsilon_r \equiv \epsilon/\epsilon_0 = 1 + \chi_e > 1$ . This is a very rudimentary example of *screening*.

### 5.1.2 The Dielectric Constant

See also [37].

The title of this section is ironic because the dielectric constant,  $\epsilon_r \equiv \epsilon/\epsilon_0$  is not constant. In fact, for time-dependent fields  $\mathbf{E}(\omega)$ , the permittivity  $\epsilon(\omega)$  depends on the frequency of the field<sup>8</sup>. Let us see how the frequency dependence arises through an example.

Earlier, we calculated the permittivity of an atom (well actually we called it  $\alpha$  then). Let us return to that model. Let us simplify the notation and denote the restoring restoring force as a harmonic oscillator

$$\mathbf{F}_{E-N} = -k_C \frac{q^2}{a^3} \mathbf{x} \equiv -m\omega_0^2 \mathbf{x}$$

with  $m$  the electronic mass and  $\omega_0$  the *resonant frequency* of the atom. We let  $m$  be the electronic mass since the electron is about 2000 times lighter than the nucleus; i.e. we assume the nucleus is stationary.

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<sup>8</sup> Here, the time-dependence is implicitly sinusoidal. For *arbitrary* time-dependence, the behaviour can be accounted for by Fourier transforming the time-dependence, calculating in  $\omega$ -space, then transforming back.

Let us let the driving force be time dependent,  $\mathbf{F}(t) = -q\mathbf{E}(t)$ . Here,  $-q$  is the electronic charge. To describe the most general case<sup>9</sup>, let's also allow for damping:  $\mathbf{F}_{\text{damp}} = -m\gamma\dot{\mathbf{x}}$ . We want to know the polarization,  $\mathbf{P}(t)$ , so we need to calculate the dynamics of the “oscillator”. The equation of motion is

$$m\ddot{\mathbf{x}} - m\gamma\dot{\mathbf{x}} + m\omega_0^2\mathbf{x} = -q\mathbf{E}(t)$$

For a sinusoidally oscillating field  $\mathbf{E}(t) = \mathbf{E}(\omega)\exp(i\omega t)$ , we expect sinusoidal oscillation  $\mathbf{x}(t) = \mathbf{x}(\omega)\exp(i\omega t)$ . Then

$$\mathbf{x}(\omega) = \frac{-q\mathbf{E}(\omega)}{-m\omega^2 - im\gamma\omega + m\omega_0^2}$$

Recalling that  $\mathbf{p} \equiv q\mathbf{d} \equiv \alpha\mathbf{E}$ , we find

$$\alpha = \frac{q^2}{m} \frac{1}{-\omega^2 - i\gamma\omega + \omega_0^2}$$

for the atomic polarizability,  $\alpha$ . It is both frequency dependent and complex so that  $\epsilon(\omega) \equiv \epsilon_1(\omega) + i\epsilon_2(\omega)$  is frequency dependent and complex. What does this mean? Well, EM waves propagating in matter have dispersion given by

$$k^2 = \mu\epsilon(\omega)\omega^2$$

$\mu$  is the magnetic permeability: let's not care about it. For complex  $\epsilon$ , the wave-vector  $\mathbf{k}$  has complex magnitude  $k = k_1 + ik_2$ . As an example, suppose that the wave-vector points along  $\hat{\mathbf{z}}$ . For non-zero imaginary part, an electric field oscillation

$$\mathbf{E}(\mathbf{x}, t) = \mathbf{E}_0(\omega)\exp(ikz) = \mathbf{E}_0(\omega)\exp(-k_2z)\exp(ik_1z)$$

is exponentially damped along its direction of propagation in matter. **I should also include conductors, etc. here but I don't need this yet so let's go work on the modern theory of polarization.**

### 5.1.3 Screening

Tong's §7.7 [73].

## 5.2 The Modern Theory of Polarization

We slipped quite a few things under the rug in the preceding section. For one, we supposed that matter could be divided into neutral “units” that could be polarized by an external field. In real crystals, the charge density is instead distributed throughout the unitcell. It is peaked near the atoms, but does *not* fall to zero in the interstitial regions. Thus, in real crystals, there is no natural way to divide space into “polarizable” units.

...

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<sup>9</sup> This is also the most physical case! In reality, the “oscillator” gains/loses energy by interacting with other atoms, radiating energy away, absorbing radiation, etc. The microscopic processes won't matter for now; the damping term will capture the qualitative behaviour we need to understand.

## 5.3 Optical Properties of Matter

If we can calculate the dielectric function  $\epsilon(\omega)$  from, e.g. DFT, then it is possible to calculate absorption and reflection spectra, energy loss, etc. [47, 63].

### 5.3.1 Misc.

See [https://people.sissa.it/~dalcorsor/lectures/electric\\_field.pdf](https://people.sissa.it/~dalcorsor/lectures/electric_field.pdf)

## 6 Propagator

The Hamiltonian operator is usually in the form of a linear differential operator. There exists a very robust and powerful way to solve linear differential equations: by *Green functions* (GF). In the framework of quantum theory, the GF often takes the name *propagator* (see below) and this is the notation we use in this section<sup>10</sup>. It can also be called the time evolution operator. The time evolution operator is well known in usual quantum mechanics. Let us recall a little about it.

This part of the derivation follows Tokmakoff [72]. Suppose the we know the state of our quantum system at time  $t_0$ . Label it by  $|\Psi(t_0)\rangle$ . We are neglecting the spatial dependence for now. What we want to know is the state at some later time,  $|\Psi(t)\rangle$  where  $t > t_0$  by assumption of causality. We define the propagator (or time evolution operator)  $\hat{U}(t, t_0)$  that acts on our state:

$$|\Psi(t)\rangle = \hat{U}(t, t_0)|\Psi(t_0)\rangle$$

We are going to try to figure out what  $\hat{U}$  is, but for now let's make some general observations.

First of all, it must be unitary if probability is to be conserved. Namely

$$\langle\Psi(t_0)|\Psi(t_0)\rangle \equiv \langle\Psi(t)|\Psi(t)\rangle = \langle\Psi(t_0)|\hat{U}^\dagger(t, t_0)\hat{U}(t, t_0)|\Psi(t_0)\rangle$$

is only satisfied if  $\hat{U}^\dagger\hat{U} \equiv 1$ , i.e. if  $\hat{U}^\dagger = \hat{U}^{-1}$ . Then we conclude that  $\hat{U}$  is unitary. We also suppose that, for this theory to make sense, it must be true that  $\hat{U}(t, t) = 1$ . i.e. the wavefunction must equal itself! We also suppose that we can *compose* time evolution operations, i.e.

$$\begin{aligned} |\Psi(t_2)\rangle &= \hat{U}(t_2, t_1)|\Psi(t_1)\rangle = \hat{U}(t_2, t_1)\hat{U}(t_1, t_0)|\Psi(t_0)\rangle \\ &= \hat{U}(t_2, t_0)|\Psi(t_0)\rangle \end{aligned}$$

where we observe that  $\hat{U}(t_2, t_1)\hat{U}(t_1, t_0) \equiv \hat{U}(t_2, t_0)$ . That this is true follow from the fact that we have left the times  $t_0$ ,  $t$  and the interval  $t - t_0$  arbitrary in the definitions above. Note that the order of the operators matters! The fact that only the time interval has been defined so far also implies  $\hat{U}(t, t_0) = \hat{U}(t - t_0)$  only depends on the difference of times. If we arbitrarily define  $t_0 = 0$ , then  $\hat{U}(t) = \hat{U}(t_2 + t_1)$ <sup>11</sup>. As a final observation, note that the inverse of the propagator is just time reversal:

$$\begin{aligned} \langle\Psi(t)|\Psi(t)\rangle &= \langle\Psi(t_0)|\hat{U}^\dagger(t - t_0)\hat{U}(t - t_0)|\Psi(t_0)\rangle = \\ &= \langle\Psi(t_0)|\left(\hat{U}^{-1}(t - t_0)|\Psi(t)\rangle\right) = \langle\Psi(t_0)|\Psi(t_0)\rangle \end{aligned}$$

where we deduce that  $\hat{U}^{-1}(t - t_0) \equiv \hat{U}(t_0 - t)$

<sup>10</sup> We use this notation (a) because it sounds cool and (b) because Altland and Simons use it [4]. Note that often times the Green function includes a multiplicative factor of  $-i$  that the propagator does not.

<sup>11</sup> This is suggestive of the functional form of these operators... we know a set of functions that share this property i.e.  $\exp(A)\exp(B) = \exp(A + B)$

## 6.1 The Equation of Motion

To find out what  $\hat{U}(t)$  is, we study its equation of motion. Let  $\delta t$  be an infinitesimal time interval. Then  $\hat{U}(t + \delta t) = \hat{U}(t) - i\hat{\Omega}(t)\delta t$ . The operator  $\hat{\Omega}$  is required to be Hermitian by the requirement that  $\hat{U}$  is unitary. Moreover, to have the correct dimensions ( $\hat{U}$  is a probability amplitude which is dimensionless),  $[\hat{\Omega}] = T^{-1}$  has dimensions of frequency. Now define  $\partial_t \hat{U}(t) \sim (\hat{U}(t + \delta t) - \hat{U}(t))/\delta t$ . We see that  $\partial_t \sim -i\hat{\Omega}(t)$ . Then we arrive at

$$\partial_t \hat{U}(t) = -i\hat{\Omega}(t)\hat{U}(t)$$

Now since  $\hat{\Omega}$  has dimensions of frequency, and in quantum mechanics,  $\omega = E/\hbar$  is a practically fundamental relation, we guess that  $\hat{\Omega} \equiv \hat{H}$  is the energy operator. So we find

$$i\hbar \partial_t \hat{U}(t) = \hat{H}\hat{U}(t) \quad (44)$$

i.e. the propagator satisfies a time-dependent Schrödinger's equation (TDSE). Obviously then multiplying by  $|\Psi(t_0)\rangle$

$$i\hbar \partial_t |\Psi(t)\rangle = \hat{H}|\Psi(t_0)\rangle$$

gives us the TDSE for the state. It's tempting, and often just claimed, that we can solve eq. 44 by separation of variables. We would find  $\hat{U}(t) \sim \exp(-i\hat{H}t)$ . However, these are operators and this method isn't necessarily valid. Let us proceed in the correct way!

Suppose instead that we integrate  $\hat{U}$  from  $t_0$  to  $t$ . Then, on the left hand side, we find

$$i\hbar \int_{t_0}^t dt' \partial_{t'} \hat{U}(t') = i\hbar [\hat{U}(t, t_0) - 1]$$

On the right hand side, without picking a particular  $\hat{H}$  and explicitly evaluating, all we can say is

$$i\hbar [\hat{U}(t, t_0) - 1] = \int_{t_0}^t dt_1 \hat{H}(t_1) \hat{U}(t_1)$$

which then, after solving for  $\hat{U}(t, t_0)$ , gives

$$\hat{U}(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t dt_1 \hat{H}(t_1) \hat{U}(t_1, t_0) \quad (45)$$

The appearance of  $\hat{U}$  in the integrand on the right is troublesome. The way forward is *iteration*. We plug eq. 45 into itself

$$\begin{aligned} \hat{U}(t, t_0) &= 1 - \frac{i}{\hbar} \int_{t_0}^t dt_1 \hat{H}(t_1) \left( 1 - \frac{i}{\hbar} \int_{t_0}^{t_1} dt_2 \hat{H}(t_2) \hat{U}(t_2, t_0) \right) \\ &= 1 - \frac{i}{\hbar} \int_{t_0}^t dt_1 \hat{H}(t_1) + \left( \frac{-i}{\hbar} \right)^2 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \hat{H}(t_1) \hat{H}(t_2) \hat{U}(t_2, t_0) \end{aligned}$$

and then we plug this back into itself, being careful at every step to maintain the correct order of the Hamiltonian operators. We can *not* move them through each other since we

don't know a-priori that they commute at different times. The next iteration is

$$\begin{aligned}\hat{U}(t, t_0) = & 1 - \frac{i}{\hbar} \int_{t_0}^t dt_1 \hat{H}(t_1) + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^t \int_{t_0}^{t_1} dt_1 dt_2 \hat{H}(t_1) \hat{H}(t_2) \\ & + \left(\frac{-i}{\hbar}\right)^3 \int_{t_0}^t \int_{t_0}^{t_1} \int_{t_0}^{t_2} dt_1 dt_2 dt_3 \hat{H}(t_1) \hat{H}(t_2) \hat{H}(t_3) \hat{U}(t_3, t_0)\end{aligned}$$

We now see a clear pattern for how to write this thing to arbitrary order.

$$\begin{aligned}\hat{U}(t, t_0) &= 1 + \sum_{n=1}^{\infty} \hat{U}^{(n)}(t, t_0) \\ \hat{U}^{(n)}(t, t_0) &= \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \hat{H}(t_1) \hat{H}(t_2) \cdots \hat{H}(t_n)\end{aligned}\tag{46}$$

Note the time ordering of the Hamiltonians;  $t_0 \leq t_1 \leq t_2 \leq \cdots t_n \leq t$ . This is physically sensible and already looks kind of like a path integral. The physical interpretation is as follows. Imagine we start in a state  $|i\rangle$  and want to find the probability amplitude for evolution into a final state  $|f\rangle$ . i.e. we intend to use  $|f\rangle = \hat{U}(t, t_0)|i\rangle = |i\rangle + \sum_n \hat{U}^{(n)}(t, t_0)|i\rangle$ . The first term,  $|i\rangle$ , is just the amplitude that the initial state propagates undisturbed for the whole interval. The second term

$$\hat{U}^{(1)}(t, t_0)|i\rangle = \frac{-i}{\hbar} \int_{t_0}^t dt_1 \hat{H}(t_1)|i\rangle$$

gives the probability that the initial state  $|i\rangle$  evolves directly into the final state  $|f\rangle$ . The remaining terms involve intermediate states. e.g.

$$\begin{aligned}\hat{U}^{(2)}(t, t_0)|i\rangle &= \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \hat{H}(t_1) \hat{H}(t_2)|i\rangle \\ &= \sum_l \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \hat{H}(t_1)|l\rangle \langle l| \hat{H}(t_2)|i\rangle\end{aligned}$$

gives the amplitude to first scatter from  $|i\rangle$  into  $|l\rangle$  then from  $|l\rangle$  into  $|f\rangle$ . The peculiar bounds on the integration, and the time ordering, are so that the causality is obeyed. The particle must first scatter into the intermediate state before the intermediate state can evolve for the rest of the interval. Higher order terms have analogous interpretations.

The cumbersome theory presented in this section so far is valid for time-dependent Hamiltonians. For a vast number of interesting physical systems, the Hamiltonian is time independent and the formalism above simplifies significantly. Specifically, for time independent Hamiltonians,  $[\hat{H}(t), \hat{H}(t')] \equiv 0$  and

$$\hat{U}^{(n)}(t, t_0) = (-i)^n \left(\frac{\hat{H}}{\hbar}\right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n$$

For convenience, shift  $t_0 \rightarrow 0$ . Then, integrating from right to left,

$$\begin{aligned} \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n &= \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-2}} dt_{n-1} t_{n-1} = \\ \frac{1}{2} \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-3}} dt_{n-2} t_{n-2}^2 &= \frac{1}{2 \cdot 3} \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-4}} dt_{n-3} t_{n-3}^3 = \\ \frac{1}{(n-2)!} \int_0^t dt_1 \int_0^{t_1} dt_2 t_2^{n-2} &= \frac{1}{(n-1)!} \int_0^t dt_1 t_1^{n-1} = \frac{t^n}{n!} \end{aligned}$$

Sticking this into eq. 46, we find

$$\hat{U}(t, t_0) = \sum_{n=0}^{\infty} \frac{(-i\hat{H}(t-t_0)/\hbar)^n}{n!} \equiv \exp\left(-i\frac{\hat{H}(t-t_0)}{\hbar}\right) \quad (47)$$

## 6.2 The Path Integral Formulation

All of the two preceding sections were informative but rather abstract. We still haven't seen, in practice, how to calculate the propagator in any particular case. So then let us now derive the propagator in another way. We first start by going to the position representation. We will stick to time independent Hamiltonians from now on. As usual, we write the wave function as  $\Psi(\mathbf{x}, t) = \langle \mathbf{x} | \Psi(t) \rangle$ . Using the definition of the propagator, this becomes  $\Psi(\mathbf{x}, t) = \langle \mathbf{x} | \hat{U}(t-t_0) | \Psi(t_0) \rangle$ . Now insert a complete set of states

$$\Psi(\mathbf{x}, t) = \int d\mathbf{x}_0 \langle \mathbf{x} | \hat{U}(t-t_0) | \mathbf{x}_0 \rangle \langle \mathbf{x}_0 | \Psi(t_0) \rangle \equiv \int d\mathbf{x}_0 U(\mathbf{x}, \mathbf{x}_0; t-t_0) \Psi(\mathbf{x}_0, t_0)$$

Thus, in the positions space representation we have determined that the propagator is, kinda obviously,  $U(\mathbf{x}, \mathbf{x}_0; t-t_0) = \langle \mathbf{x} | \hat{U}(t-t_0) | \mathbf{x}_0 \rangle$ . Note that, from eq. 47 above, we can write

$$\begin{aligned} U(\mathbf{x}, \mathbf{x}_0; t-t_0) &= \sum_n \langle \mathbf{x} | \exp\left(-i\frac{\hat{H}(t-t_0)}{\hbar}\right) | n \rangle \langle n | \mathbf{x}_0 \rangle = \\ \sum_n \exp\left(-i\frac{E_n(t-t_0)}{\hbar}\right) \langle \mathbf{x} | n \rangle \langle n | \mathbf{x}_0 \rangle &= \sum_n \exp\left(-i\frac{E_n(t-t_0)}{\hbar}\right) \psi_n(\mathbf{x}) \psi_n^*(\mathbf{x}_0) \end{aligned}$$

The  $\psi_n(\mathbf{x})$  are the eigenfunctions of  $\hat{H}$ , so assuming that we can solve the TISE, we can study the time evolution. Unfortunately solving the TISE is usually not so easy, so let us look for yet another way to write the propagator.

First, let  $t_0 \rightarrow 0$  for convenience later. We will split the total interval,  $t$ , into  $N$  chunks that are each  $\epsilon = t/N$  long. i.e.  $\exp(-i\hat{H}t/\hbar) \equiv [\exp(-i\hat{H}\epsilon/\hbar)]^N$ . We will take the limit  $N \rightarrow \infty$  later, so consider  $\epsilon$  as infinitesimal. The propagator is now written

$$\begin{aligned} U(\mathbf{x}, \mathbf{x}_0; t) &= \langle \mathbf{x} | [\exp(-i\hat{H}\epsilon/\hbar)]^N | \mathbf{x}_0 \rangle = \\ \langle \mathbf{x} | \exp(-i\hat{H}\epsilon/\hbar) \exp(-i\hat{H}\epsilon/\hbar) \cdots \exp(-i\hat{H}\epsilon/\hbar) | \mathbf{x}_0 \rangle \end{aligned}$$

Between each one, insert “unity”

$$\hat{1} = \int d\mathbf{p}_i d\mathbf{x}_i | \mathbf{x}_i \rangle \langle \mathbf{x}_i | \mathbf{p}_i \rangle \langle \mathbf{p}_i |$$

The result is

$$U(\mathbf{x}, \mathbf{x}_0; t) = \int d\mathbf{x}_1 d\mathbf{p}_1 \cdots d\mathbf{x}_N d\mathbf{p}_N \langle \mathbf{x} | \mathbf{x}_N \rangle \langle \mathbf{x}_N | \mathbf{p}_N \rangle \langle \mathbf{p}_N | \exp(-i\hat{H}\epsilon/\hbar) | \mathbf{x}_{N-1} \rangle \times \\ \langle \mathbf{x}_{N-1} | \mathbf{p}_{N-1} \rangle \langle \mathbf{p}_{N-1} | \exp(-i\hat{H}\epsilon/\hbar) \cdots | \mathbf{x}_1 \rangle \langle \mathbf{x}_1 | \mathbf{p}_1 \rangle \langle \mathbf{p}_1 | \exp(-i\hat{H}\epsilon/\hbar) | \mathbf{x}' \rangle$$

The integrand is a product of many matrix elements, each of the form

$$\langle \mathbf{x}_{i+1} | \mathbf{p}_{i+1} \rangle \langle \mathbf{p}_{i+1} | \exp(-i\hat{H}\epsilon/\hbar) | \mathbf{x}_i \rangle$$

To lowest order in  $\epsilon$ , which will be exact in the limit  $N \rightarrow \infty$ <sup>12</sup>.

$$\langle \mathbf{p}_{i+1} | \exp(-i\hat{H}\epsilon/\hbar) | \mathbf{x}_i \rangle \approx \langle \mathbf{p}_{i+1} | \mathbf{x}_i \rangle \exp \left( -i \left[ \frac{p_{i+1}^2}{2m_e} + V(\mathbf{x}_i) \right] \frac{\epsilon}{\hbar} \right)$$

Use the result that  $\langle \mathbf{x} | \mathbf{p} \rangle \equiv (2\pi\hbar)^{3/2} \exp(i\mathbf{p} \cdot \mathbf{x}/\hbar)$  (here  $\mathbf{p}$  is momentum, not a wave number!). Then the whole matrix element is

$$\langle \mathbf{x}_{i+1} | \mathbf{p}_{i+1} \rangle \langle \mathbf{p}_{i+1} | \mathbf{x}_i \rangle \exp \left( -i \left[ \frac{p_{i+1}^2}{2m_e} + V(\mathbf{x}_i) \right] \frac{\epsilon}{\hbar} \right) = \\ \frac{1}{(2\pi\hbar)^3} \exp \left( -\frac{i\epsilon}{\hbar} \left[ \frac{p_{i+1}^2}{2m_e} + V(\mathbf{x}_i) - \mathbf{p}_{i+1} \cdot \frac{(\mathbf{x}_{i+1} - \mathbf{x}_i)}{\epsilon} \right] \right)$$

and the propagator is written as

$$U(\mathbf{x}, \mathbf{x}_0; t) = \int_{\mathbf{x}_0}^{\mathbf{x}} \prod_i^{N-1} \prod_j^N \frac{d\mathbf{x}_i d\mathbf{p}_j}{(2\pi\hbar)^3} \exp \left( -\frac{i\epsilon}{\hbar} \sum_k^{N-1} \left[ \frac{p_{k+1}^2}{2m_e} + V(\mathbf{x}_k) - \mathbf{p}_{k+1} \cdot \frac{(\mathbf{x}_{k+1} - \mathbf{x}_k)}{\epsilon} \right] \right)$$

Note that there are only  $N - 1$  space integrals; this is because the integral over the term  $\langle \mathbf{x} | \mathbf{x}_N \rangle = \delta(\mathbf{x} - \mathbf{x}_N)$  selects the upper boundary condition. If we assume that potentials are always momentum independent, then we can integrate over momentum once and for all. All momentum integrals are Gaussian and can be done willy-nilly

$$U(\mathbf{x}, \mathbf{x}_0; t) = \left( \frac{m}{2\pi i \epsilon \hbar} \right)^{3N/2} \int_{\mathbf{x}_0}^{\mathbf{x}} \prod_i^{N-1} d\mathbf{x}_i \exp \left( \frac{i\epsilon}{\hbar} \sum_k^{N-1} \left[ \frac{m_e}{2} \left( \frac{\mathbf{x}_{k+1} - \mathbf{x}_k}{\epsilon} \right)^2 - V(\mathbf{x}_k) \right] \right) \quad (48)$$

Finally, we take the limit  $N \rightarrow \infty$ . Then  $\epsilon \rightarrow t'$  become a continuous coordinate and  $(\mathbf{x}_{k+1} - \mathbf{x}_k)/\epsilon \rightarrow (\mathbf{x}(t' + \delta t') - \mathbf{x}(t'))/\delta t' = \dot{\mathbf{x}}$ . Moreover, the sum in the integrand becomes an integral

$$\sum_k^{N-1} \epsilon \rightarrow \int_0^t dt'$$

and finally, we define

$$\left( \frac{m}{2\pi i \epsilon \hbar} \right)^{3N/2} \prod_i^{N-1} d\mathbf{x}_i \equiv \mathcal{D}\mathbf{x}$$

<sup>12</sup> Use the Baker-Campbell-Hausdorff formula and drop all terms larger than  $O(\epsilon^2)$  in  $\epsilon$ . Then each operator  $\exp(-i\hat{T}\epsilon/\hbar)$  acts on the momentum eigenstates and the operators  $\exp(-i\hat{V}\epsilon/\hbar)$  act on the position eigenstates.



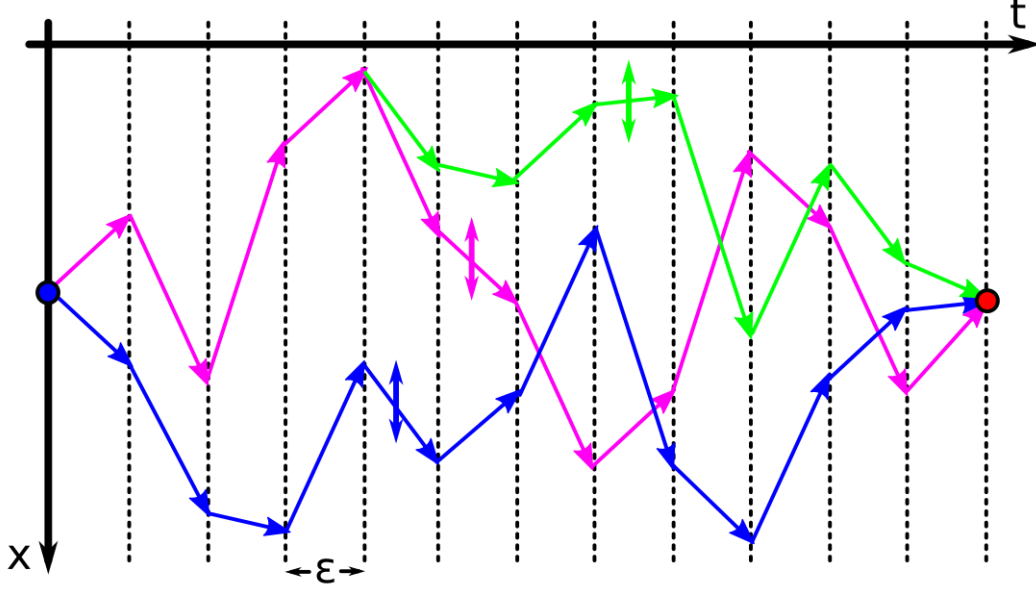


Fig. 4: “Sum over paths” interpretation of the path integral. The horizontal axis is time, divided into slices of width  $\epsilon$ . The different colored paths label different “trajectories” that the system can take.

The fact that this is divergent doesn’t matter in practice! So then the path integral is written (relabeling some variables because of poor management earlier)

$$U(\mathbf{x}_f, \mathbf{x}_i; T) = \int_{\mathbf{x}(0)=\mathbf{x}_f}^{\mathbf{x}(T)=\mathbf{x}_i} \mathcal{D}\mathbf{x}(t) \exp \left( \frac{i}{\hbar} \int_0^T dt \left[ \frac{m_e}{2} \dot{\mathbf{x}}^2(t) - V(\mathbf{x}(t)) \right] \right) \quad (49)$$

The integral in the action is just the classical action,  $S[\mathbf{x}(t)] = \int_0^T dt L(\mathbf{x}, \dot{\mathbf{x}})$ , with  $L(\mathbf{x}, \dot{\mathbf{x}}) = m_e \dot{\mathbf{x}}^2/2 - V(\mathbf{x}(t))$  the Lagrangian. In this (very common) notation,

$$U(\mathbf{x}_f, \mathbf{x}_i; T) = \int_{\mathbf{x}(0)=\mathbf{x}_i}^{\mathbf{x}(T)=\mathbf{x}_f} \mathcal{D}\mathbf{x}(t) \exp \left( \frac{i}{\hbar} S[\mathbf{x}(t)] \right)$$

### 6.2.1 Path Integral Propagator (Redux)

Let us re-derive the path integral expression for the propagator in a different way. This alternative way follows Gurarie’s notes [32]. Start from the expression

$$\Psi(\mathbf{x}, t) = \int d\mathbf{x}_0 U(\mathbf{x}, \mathbf{x}_0; t) \Psi(\mathbf{x}_0, t_0)$$

Just like before, we can use the composition property of the propagator and split time into  $N$  chunks with each infinitesimal propagator evolving the wave function forward in time and amount  $\epsilon = t/N$ .

$$\Psi(\mathbf{x}, t) = \int d\mathbf{x}_0 d\mathbf{x}_1 \cdots d\mathbf{x}_{N-1} U(\mathbf{x}, \mathbf{x}_{N-1}; \epsilon) \cdots U(\mathbf{x}_1, \mathbf{x}_0; \epsilon) \Psi(\mathbf{x}_0, t_0)$$

This is a physically transparent form! See fig. 4. For each tiny slice of time propagation, we have to account for the non-zero probability that the wave function takes *any* path through space; in other words, we have to sum up the probabilities of all the possible ways that a particle, initially at  $\mathbf{x}_i$ , can propagate to  $\mathbf{x}_f$ . It could take the blue path in the figure, or the pink path, or start down the pink path and split off and take the green path later; *or* any number of other possibilities. This sounds preposterous, but in quantum mechanics, it is a fact we have to deal with! More over, due to the wave like nature of quantum particles, the path integral accounts for the fact that the particle takes *all* of these paths simultaneously. The  $\sim \exp(-i\hat{H}/\hbar)$  factor is the probability amplitude for a particular path. How do we get this to work in practice?

Recall that each of the propagators has to satisfy an equation of motion, eq. 45.

$$i\hbar\partial_t U(\mathbf{x}_f, \mathbf{x}_i; t) = \hat{H}U(\mathbf{x}_f, \mathbf{x}_i; t)$$

We also need the boundary condition for  $t_f \rightarrow t_0$ . Obviously for a wave function that doesn't propagate forward in time must equal itself... Then

$$\begin{aligned} \lim_{t_f \rightarrow t_i} \Psi(\mathbf{x}_f, t_f - t_i) &= \Psi(\mathbf{x}_i, t_i) = \\ \lim_{t_f \rightarrow t_i} \int d\mathbf{x}_i U(\mathbf{x}_f, \mathbf{x}_i; t_f - t_i) \Psi(\mathbf{x}_i, t_i) &= \int d\mathbf{x}_i \delta(\mathbf{x}_f - \mathbf{x}_i) \Psi(\mathbf{x}_i, t_i) \end{aligned}$$

So we conclude that

$$\lim_{t_f \rightarrow t_i} U(\mathbf{x}_f, \mathbf{x}_i; t_f - t_i) = \delta(\mathbf{x}_f - \mathbf{x}_i)$$

On the left hand side of the equation of motion, we can write

$$i\hbar\partial_t U(\mathbf{x}_f, \mathbf{x}_i; t) \approx i\hbar \frac{U(\mathbf{x}_f, \mathbf{x}_i; \epsilon) - U(\mathbf{x}_f, \mathbf{x}_i; 0)}{\epsilon} = \frac{i\hbar}{\epsilon} U(\mathbf{x}_f, \mathbf{x}_i; \epsilon) - \frac{i\hbar}{\epsilon} \delta(\mathbf{x}_f - \mathbf{x}_i)$$

and on the right side

$$\hat{H}U(\mathbf{x}_f, \mathbf{x}_i; 0) = \hat{H}\delta(\mathbf{x}_f - \mathbf{x}_i)$$

Then

$$\begin{aligned} \frac{i\hbar}{\epsilon} U(\mathbf{x}_f, \mathbf{x}_i; \epsilon) &= \frac{i\hbar}{\epsilon} \left( 1 - \frac{i\epsilon}{\hbar} \hat{H} \right) \delta(\mathbf{x}_f - \mathbf{x}_i) \\ &= \frac{i}{\epsilon} \int \frac{d\mathbf{p}}{2\pi} \left( 1 - \frac{i\epsilon}{\hbar} \hat{H} \right) \exp(i\mathbf{p} \cdot (\mathbf{x}_f - \mathbf{x}_i)/\hbar) \end{aligned}$$

Now let the Hamiltonian operator act of the coordinates<sup>13</sup>.

$$\begin{aligned} &\frac{i}{\epsilon} \int \frac{d\mathbf{p}}{2\pi} \left( 1 - \frac{i\epsilon}{\hbar} \left[ \frac{p^2}{2m_e} + V(\mathbf{x}_f) \right] \right) \exp(i\mathbf{p} \cdot (\mathbf{x}_f - \mathbf{x}_i)/\hbar) \\ &\approx \frac{i}{\epsilon} \int \frac{d\mathbf{p}}{2\pi} \exp \left( -\frac{i\epsilon}{\hbar} \left[ \frac{p^2}{2m_e} + V(\mathbf{x}_f) - \mathbf{p} \cdot \frac{\mathbf{x}_f - \mathbf{x}_i}{\epsilon} \right] \right) \end{aligned}$$

We've encountered essentially the same expression before. We can integrate over  $\mathbf{p}$  and put everything together. The result is eq. 49.

<sup>13</sup> Note that we can use either  $V(\mathbf{x}_f)$  or  $V(\mathbf{x}_i)$  since  $\mathbf{x}_i$  and  $\mathbf{x}_f$  are only infinitesimally far apart in the limit  $N \rightarrow \infty$ . See §3.2 in [4].

### 6.3 Partition Function by Path Integrals

Let us now extend the technicalities of the last section to a seemingly completely unrelated topic. Recall that in equilibrium, just about everything can be calculated from the partition function of statistical mechanics. Let's only consider the full quantum treatment here. The quantum mechanical partition function for an arbitrary Hamiltonian in the canonical ensemble is

$$Z(T) = \text{tr}[\exp(-\beta\hat{H})] \quad (50)$$

with  $\beta = 1/(k_B T)$ .  $T$  is temperature and  $k_B$  is Boltzmann's constant, and  $\text{tr}$  is the trace operator. Recall that the trace is basis independent, so let's pick a convenient basis and evaluate it the partition function. Suppose we work in the energy eigenbasis:

$$Z(T) = \sum_{\alpha} \langle \alpha | \exp(-\beta\hat{H}) | \alpha \rangle = \sum_{\alpha} \exp(-\beta\mathcal{E}_{\alpha})$$

It turns out to be pretty easy to evaluate it if we know the eigenstates, but that means solving for the eigenstates... which is hard. In particular, it's *very* hard in the many body problem. Let's try it in the position basis.

$$Z(T) = \int d\mathbf{x} \langle \mathbf{x} | \exp(-\beta\hat{H}) | \mathbf{x} \rangle$$

It's still hard to evaluate this, but it's a jumping off point. We split  $\beta$  into  $N$  pieces with  $\epsilon \equiv \hbar\beta/N$ <sup>14</sup>. Then the Boltzmann weight is

$$\exp(-\beta\hat{H}) = \exp(-\epsilon\hat{H}/\hbar) \exp(-\epsilon\hat{H}/\hbar) \exp(-\epsilon\hat{H}/\hbar) \cdots$$

This works because  $\hat{H}$  commutes with its self. The partition function is

$$Z(T) = \int d\mathbf{x} \langle \mathbf{x} | \exp(-\epsilon\hat{H}/\hbar) \exp(-\epsilon\hat{H}/\hbar) \cdots \exp(-\epsilon\hat{H}/\hbar) | \mathbf{x} \rangle$$

We want to insert “unity” in many places. For unity, we will use

$$\begin{aligned} \hat{1} &= \int d\mathbf{x}_i |\mathbf{x}_i\rangle \langle \mathbf{x}_i| \\ \hat{1} &= \int d\mathbf{p}_i |\mathbf{p}_i\rangle \langle \mathbf{p}_i| \end{aligned}$$

Put a position one on the right side of every Boltzmann piece and a momentum one on the left.

$$\begin{aligned} Z(T) &= \int d\mathbf{x} d\mathbf{x}_1 d\mathbf{p}_1 \cdots d\mathbf{x}_N d\mathbf{p}_N \langle \mathbf{x} | \mathbf{p}_N \rangle \langle \mathbf{p}_N | \exp(-\epsilon\hat{H}/\hbar) | \mathbf{x}_N \rangle \cdots \\ &\quad \langle \mathbf{p}_2 | \exp(-\epsilon\hat{H}/\hbar) | \mathbf{x}_2 \rangle \langle \mathbf{x}_2 | \mathbf{p}_1 \rangle \langle \mathbf{p}_1 | \exp(-\epsilon\hat{H}/\hbar) | \mathbf{x}_1 \rangle \langle \mathbf{x}_1 | \mathbf{x} \rangle \end{aligned}$$

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<sup>14</sup> I don't know why  $\hbar$  is introduced here, but this is the convention everywhere in the literature that I have looked.

The integrand is a product of many matrix elements, each of the form

$$\langle \mathbf{x}_{i+1} | \mathbf{p}_i \rangle \langle \mathbf{p}_i | \exp(-\epsilon \hat{H}/\hbar) | \mathbf{x}_i \rangle$$

Let's assume the Hamiltonian is just a single particle quantum mechanical Hamiltonian for now. To lowest order in  $\epsilon$ , which will be exact in the limit  $N \rightarrow \infty$

$$\langle \mathbf{p}_i | \exp(-\epsilon \hat{H}/\hbar) | \mathbf{x}_i \rangle \approx \exp\left(-\frac{\epsilon}{\hbar} \left[ \frac{p_i^2}{2m} + V(\mathbf{x}_i) \right]\right) \langle \mathbf{p}_i | \mathbf{x}_i \rangle$$

Then the whole matrix element is

$$\langle \mathbf{x}_{i+1} | \mathbf{p}_i \rangle \langle \mathbf{p}_i | \exp(-\epsilon \hat{H}/\hbar) | \mathbf{x}_i \rangle \approx \frac{1}{(2\pi\hbar)^3} \exp\left(-\frac{\epsilon}{\hbar} \left[ \frac{p_i^2}{2m} + V(\mathbf{x}_i) - \frac{i}{\epsilon} \mathbf{p}_i \cdot (\mathbf{x}_{i+1} - \mathbf{x}_i) \right]\right)$$

Stick these into the partition function and the whole thing becomes

$$Z(T) = \lim_{N \rightarrow \infty} \int d\mathbf{x} \left( \prod_i^N \frac{d\mathbf{x}_i d\mathbf{p}_i}{(2\pi\hbar)^3} \right) \times \\ \exp\left(-\frac{\epsilon}{\hbar} \sum_j^N \left[ \frac{p_j^2}{2m} + V(\mathbf{x}_j) - i\mathbf{p}_j \cdot \frac{(\mathbf{x}_{j+1} - \mathbf{x}_j)}{\epsilon} \right]\right) \langle \mathbf{x}_1 | \mathbf{x} \rangle$$

and we have to note that  $\mathbf{x}_{N+1} = \mathbf{x}$  in the sum. This is from  $\langle \mathbf{x} | \mathbf{p}_N \rangle$  in the integrand. The position matrix element on the right is  $\langle \mathbf{x}_1 | \mathbf{x} \rangle = \delta(\mathbf{x}_1 - \mathbf{x})$ , which allows us to do the integral over  $\mathbf{x}$ . Ultimately the result for the partition function is

$$Z(T) = \lim_{N \rightarrow \infty} \int \prod_i^N \frac{d\mathbf{x}_i d\mathbf{p}_i}{(2\pi\hbar)^3} \exp\left(-\frac{\epsilon}{\hbar} \sum_j^N \left[ \frac{p_j^2}{2m} + V(\mathbf{x}_j) - i\mathbf{p}_j \cdot \frac{(\mathbf{x}_{j+1} - \mathbf{x}_j)}{\epsilon} \right]\right)$$

Introduce a new coordinate  $\tau(j) = j\epsilon = j\beta/N$  which specifies a position on the “line” of points  $\epsilon, 2\epsilon, 3\epsilon, \dots$ . Also define  $\mathbf{x}_j = \mathbf{x}(j\epsilon) \equiv \mathbf{x}(\tau)$ . From  $\langle \mathbf{x} | \mathbf{p}_N \rangle$  and  $\langle \mathbf{x}_1 | \mathbf{x} \rangle$ , we require that  $\mathbf{x}(0) = \mathbf{x}(\tau) \equiv \mathbf{x}$ , i.e. there are periodic boundary conditions on the positions in the “action”. The “circle” formed by  $\tau$  is called the “thermal-circle.” In the limit that  $N \rightarrow \infty$ ,  $\epsilon \equiv d\tau$  becomes continuous and the sum

$$\lim_{N \rightarrow \infty} \frac{\epsilon}{\hbar} \sum_j \rightarrow \frac{1}{\hbar} \int_0^\beta d\tau$$

In a similar way, the quantity  $(\mathbf{x}_{j+1} - \mathbf{x}_j)/\epsilon \equiv \partial \mathbf{x}(\tau)/\partial \tau$ . Last thing is to introduce the notation

$$\lim_{N \rightarrow \infty} \prod_i^N \frac{d\mathbf{x}_i d\mathbf{p}_i}{(2\pi\hbar)^3} \equiv \mathcal{D}\mathbf{x} \mathcal{D}\mathbf{p}$$

So finally, everything in the exponential is re-written as

$$Z(T) = \int \mathcal{D}\mathbf{x} \mathcal{D}\mathbf{p} \exp\left(-\frac{1}{\hbar} \int_0^\beta d\tau \left[ \frac{p^2(\tau)}{2m} + V(\mathbf{x}(\tau)) - i\mathbf{p}(\tau) \cdot \frac{\partial \mathbf{x}(\tau)}{\partial \tau} \right]\right)$$

This really is just a formal way of rewriting eq. 50. For every  $\tau$  in the exponential, we have to integrate over every possible position and momentum. Alternatively, for every possible configuration of the system (set by positions and momentum), we have to integrate over all  $\tau$ . This is almost useful. Let's assume we will never study momentum-dependent potentials so that we can integrate out momentum once and for all.

All of the momentum integrals are Gaussian and can be done willy-nilly

$$\int \frac{d\mathbf{p}_j}{(2\pi\hbar)^3} \exp\left(-\frac{\epsilon}{\hbar} \left[ \frac{p_j^2}{2m} - i\mathbf{p}_j \cdot \frac{(\mathbf{x}_{j+1} - \mathbf{x}_j)}{\epsilon} \right]\right) = \left(\frac{m}{2\pi\epsilon\hbar}\right)^{3/2} \exp\left(-\frac{m(\mathbf{x}_{j+1} - \mathbf{x}_j)^2}{2\epsilon\hbar}\right)$$

Sticking this back into the partition function, we arrive at

$$Z(T) = C \int_{\mathbf{x}(0)=\mathbf{x}(\beta)} \mathcal{D}\mathbf{x} \exp\left(-\frac{1}{\hbar} \int_0^\beta d\tau \left[ \frac{m}{2} \left( \frac{\partial \mathbf{x}(\tau)}{\partial \tau} \right)^2 + V(\mathbf{x}(\tau)) \right]\right)$$

with  $C = (m/2\pi\epsilon\hbar)^{3N/2}$ . In the limit  $N \rightarrow \infty$ ,  $C$  diverges. But recall how things are calculated from the partition function. For instance, the expectation value of some observable is

$$\langle O \rangle = \frac{C}{Z(T)} \int \mathcal{D}\mathbf{x} O(\mathbf{x}) \exp\left(-\frac{1}{\hbar} \int_0^\beta d\tau \left[ \frac{m}{2} \left( \frac{\partial \mathbf{x}(\tau)}{\partial \tau} \right)^2 + V(\mathbf{x}(\tau)) \right]\right)$$

Clearly the divergent  $C$  is cancelled by the normalization by  $Z(T)$  its self. So from now on, lets just forget about the  $C$ . So finally, the partition function for a quantum mechanical particle is

$$\boxed{\begin{aligned} Z(T) &= \int_{\mathbf{x}(0)=\mathbf{x}(\beta)} \mathcal{D}\mathbf{x}(\tau) \exp\left(-\frac{S_E[\mathbf{x}(\tau)]}{\hbar}\right) \\ S_E[\mathbf{x}(\tau)] &= \int_0^\beta d\tau \left( \frac{m}{2} \left( \frac{\partial \mathbf{x}}{\partial \tau} \right)^2 + V(\mathbf{x}(\tau)) \right) \end{aligned}} \quad (51)$$

$S_E[\mathbf{x}(\tau)]$  is called the *Euclidean action* as compared to the action in eq. 49, which we call the *Minkowskian action*<sup>15</sup>.

### 6.3.1 Transition Amplitude

Note the obvious similarities between eq. 51 and eq. 49. The two are related by the *Wick rotation*  $t \rightarrow -i\tau$ . The term “rotation” is due to the fact the we change “direction” in the complex plane. Really, this is just analytic continuation.

The partition function path integral is evaluated in imaginary time; the transition amplitude path integral is evaluated in real time. Apparently it's hard to solve the real time propagation on a computer (since it's oscillatory), but the the partition function path integral is over a real and exponentially decaying function. That means it can be integrated by Monte-Carlo sampling! The unfortunate trade-off is that eq. 51 loses all information about the dynamics of the system! This isn't a new challenge; in equilibrium statistical mechanics, we *always* average out the dynamics.

<sup>15</sup> This name is due to the prevalent use of the path integral in relativistic QFT; the topology of the space-time manifold in relativity is called *Minkowskian*

## 6.4 Green Functions

For more info, see [24] and [19]. The standard definition of the *Green function* (GF) differs only subtly from the propagator. The retarded Green function satisfies the equation of motion and boundary condition

$$\begin{aligned} i\hbar\partial_t G^R(\mathbf{x}_f, \mathbf{x}_i; t) &= \hat{H}G^R(\mathbf{x}_f, \mathbf{x}_i; t) \quad t > 0 \\ \lim_{t \rightarrow 0} G^R(\mathbf{x}_f, \mathbf{x}_i; t) &= -\frac{i}{\hbar}\delta(\mathbf{x}_f - \mathbf{x}_i) \end{aligned}$$

The superscript  $R$  denotes this as the retarded GF (RGF); by definition, it is only defined for  $t \geq 0$ . For  $t < 0$ , we assume  $G^R(\mathbf{x}_f, \mathbf{x}_i; t) = 0$ . The requirement that it be zero for  $t < 0$  is to enforce causality; we more-or-less swept this under the rug earlier when studying the propagator. The derivation of most quantities for the propagator are nearly identical. e.g.

$$\Psi(\mathbf{x}_f, t_f) = i\hbar \int d\mathbf{x}_0 G^R(\mathbf{x}_f, \mathbf{x}_i; t_f - t_0) \Psi(\mathbf{x}_0, t_0)$$

Apparently the RGF is related to the propagator by  $G^R(\mathbf{x}_f, \mathbf{x}_i; t) = -iU(\mathbf{x}_f, \mathbf{x}_i; t)/\hbar$ . Then

$$G^R(\mathbf{x}_f, \mathbf{x}_i; t) = -\frac{i}{\hbar} \sum_n \exp(-iE_n t/\hbar) \psi_n(\mathbf{x}_f) \psi_n^*(\mathbf{x}_i)$$

The Fourier transform (in time) of the RGF is given by

$$\begin{aligned} G^R(\mathbf{x}_f, \mathbf{x}_i; E) &= \int_0^\infty dt G^R(\mathbf{x}_f, \mathbf{x}_i; t) \exp(iEt/\hbar) = \\ &= -\frac{i}{\hbar} \sum_n \psi_n(\mathbf{x}_f) \psi_n^*(\mathbf{x}_i) \int_0^\infty dt \exp(i(E - E_n)t/\hbar) \end{aligned}$$

Let  $E - E_n \equiv \Omega$  for convenience. Taking the anti-derivative, we find

$$\int_0^\infty dt \exp(i\Omega t/\hbar) = -\frac{i\hbar}{\Omega} \left[ \lim_{t \rightarrow \infty} \exp(i\Omega t/\hbar) - 1 \right]$$

This only converges if we let  $\Omega \rightarrow \Omega + i\delta$  be complex. The convergence of this integral requires special consideration. If  $t > 0$ , then we require  $\delta > 0$  for the integral to converge. On the other hand, if  $t < 0$ , then we require  $\delta < 0$ . The distinction between *retarded* and *advanced* GF depends on which part of the complex plane we are in! The retarded GF has  $\delta > 0$  while the advanced GF has  $\delta < 0$ .

Note that  $E_n$  is real (since  $\hat{H}$  is Hermitian), so that means we are defining  $E$  to be complex. If we resolve to remember this rule, we can write

$$G^R(\mathbf{x}_f, \mathbf{x}_i; E) = \sum_n \frac{\psi_n(\mathbf{x}_f) \psi_n^*(\mathbf{x}_i)}{E - E_n + i\delta} \quad (52)$$

This is a neat result! We see that the GF contains the eigenvalues of the Hamiltonian as its poles. So if we can calculate somehow calculate the GF, we can, in principle, determine

the energy spectrum of the quantum system! Importantly, this result is independent of representation. We can prove this by noting the following

$$(E + i\delta - \hat{H})G^R(\mathbf{x}_f, \mathbf{x}_i; E) = \sum_n \psi_n(\mathbf{x}_f)\psi_n^*(\mathbf{x}_i) = \delta(\mathbf{x}_f - \mathbf{x}_i)$$

and deducing that the RGF is the inverse of the operator  $(\omega + i\delta - \hat{H})$ . (see Chp. 1 in ref. [24] for a more detailed derivation). More generally, we can write

$$\hat{G}^R(E) = \frac{1}{E + i\delta - \hat{H}} \quad (53)$$

which is valid in any representation. In most applications, it will be essential to take the limit  $\delta \rightarrow 0$ . When we do so, we have to recall whether or not we are calculating the advanced or retarded GF. We denote  $\lim_{\delta \rightarrow 0^\pm} \hat{G}^{R/A}$  by

$$\hat{G}^{R/A}(E) = \frac{1}{E \pm i0 - \hat{H}}$$

#### 6.4.1 Path Integral Formulation of the Green Function

Recalling that  $G^R(\mathbf{x}, \mathbf{y}; t) = -iU(\mathbf{x}, \mathbf{y}; t)/\hbar$ , we can simply write down the path integral RGF by multiplying eq. 49 by  $-i/\hbar$ .

### 6.5 Dyson Equation

The algebraic expression for the RGF (we will only consider retarded GF's here, so drop the  $R$ ) in eq. 53 allows us to derive an interesting equation. Suppose we have an exactly solvable model characterized by the Hamiltonian  $\hat{H}_0$ . To this we add a “perturbation”  $\hat{V}$ . Then  $\hat{H} = \hat{H}_0 + \hat{V}$  and

$$\hat{G} = \frac{1}{\omega + i\delta - \hat{H}} = \frac{1}{E + i\delta - \hat{H}_0 - \hat{V}} = \frac{1}{\hat{G}_0^{-1}(E) - \hat{V}}$$

where

$$\hat{G}_0^{-1} = E + i\delta - \hat{H}_0$$

is the “free propagator” that we can easily calculate. For convenience, we are dropping the explicit dependence on  $E$ . Then

$$\hat{G}^{-1} = \hat{G}_0^{-1} - \hat{V}$$

Hitting this on the left with  $\hat{G}_0$  and the right with  $\hat{G}$ , we have

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G}$$

By iterating this, we can write

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G}_0 + \hat{G}_0 \hat{V} \hat{G}_0 \hat{V} \hat{G}_0 + \dots$$

Defining the “T-matrix,” we have

$$\hat{T} = \hat{V} \sum_n \left[ \hat{G}_0 \hat{V} \right]^n$$

$$\hat{G} = \hat{G}_0 + \hat{G}_0 \hat{T} \hat{G}_0$$

Let  $\hat{V} = \lambda \delta(\mathbf{x} - \mathbf{x}')$  be the delta function potential and find the bound-state as the pole of the Green function.



## 7 Many-Body Physics

The discussion follows Chp. 1 of Mahan [50], but also see Ziman [86] and Chp. 2- of Altland and Simons [4]. Let's start with second-quantization. In quantum mechanics, first quantization amounts to imposing commutation relations on operators. E.g. for position and momentum

$$[\hat{x}, \hat{p}] = i\hbar$$

Do §1.1 and 1.2 in Mahan [50] and Chp. 1 and 2 in Ziman [86].

### 7.1 Identical Particles

This follows Martin [51] and Leo [61]. A particle has a set of properties: intrinsic and extrinsic. Intrinsic properties are e.g. mass, charge. Extrinsic properties are those that depend on the state: e.g. position, momentum, and spin expectation values. Identical (or “indistinguishable”) particles are those that have the same *intrinsic* properties. In math,  $N$  particles are identical if expectation values of observables are unchanged when particle's coordinates  $(\mathbf{r}_i, \mathbf{p}_i, \sigma_i, \dots)$  are swapped.

For example, consider the energy of a system of non-interacting particles:

$$\mathcal{E}_{KE} = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle = \sum_i^N \frac{p_i^2}{2m}$$

Obviously if two momenta are swapped,  $\mathcal{E}$  is unchanged. The same reasoning extends to symmetric potentials. e.g. the Coulomb interaction between a pair of charged particles

$$U(|\mathbf{r}_i - \mathbf{r}_j|) = k \frac{(eZ)^2}{|\mathbf{r}_i - \mathbf{r}_j|} = k \frac{(eZ)^2}{|\mathbf{r}_j - \mathbf{r}_i|} = U(|\mathbf{r}_j - \mathbf{r}_i|)$$

is invariant. So we see that particles should be regarded as indistinguishable in interacting quantum systems too. Since the intrinsic properties mass  $m$  and charge  $eZ$  are the same, we can't tell *which* particle is where or has what momentum by measuring an observable. This is in contrast to classical physics: given boundary conditions, we can in-principle integrate the equations of motion and track a particle's position and momentum.

Let's look at a consequence of this. Let  $\mathbf{x} = \{\mathbf{r}, \sigma\}$  be a composite coordinate that includes position and spin orientation. The expectation value in position representation (integrating over  $\mathbf{x}$  implicitly includes summing over spin) is

$$\langle \Psi | \hat{\mathcal{H}} | \Psi \rangle = \int d\mathbf{x}_1 \cdots d\mathbf{x}_N \Psi^*(\mathbf{x}_1, \dots, \mathbf{x}_N) \hat{\mathcal{H}} \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$$

Define the permutation operator  $\hat{\mathcal{P}}$  which acts on a many-body wave-function by swapping a pair of coordinates

$$\hat{\mathcal{P}} \Psi(\mathbf{x}_1, \dots, \mathbf{x}_i, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N) = \Psi(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N)$$

What's  $\alpha$ ? Since expectation values can't change

$$\langle \Psi | \hat{\mathcal{P}}^\dagger \hat{\mathcal{H}} \hat{\mathcal{P}} | \Psi \rangle = |\alpha|^2 \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle$$

We find that swapping a pair of particle's coordinates can only change the wave-function by a phase. It turns out for *Fermions* which have spin  $s = 1/2, 3/2, 5/2, \dots$  that  $\alpha = -1$ , and for *Bosons* which have  $s = 0, 1, 2, \dots$  that  $\alpha = 1$ <sup>16</sup>

## 7.2 N-Particle Wave-functions

The discussion follows Martin [51]. The many-body wave-function for  $N$  particles  $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$  has a similar physical interpretation as the single-particle wave-function in quantum mechanics. In quantum mechanics,  $\rho(\mathbf{x}) = |\psi(\mathbf{x})|^2 d\mathbf{x}$  is the probability density to find the particle in the volume  $d\mathbf{x}$ . Integrating over all space,  $\int d\mathbf{x} \rho(\mathbf{x}) = 1$  is the total-probability of observing the particle; by definition it's 1. The many-body generalization is

$$|\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)|^2 d\mathbf{x}_1 \dots d\mathbf{x}_N$$

which is the probability of simultaneously finding a particle in the volume  $d\mathbf{x}_1$  while another particle is in the volume  $d\mathbf{x}_2 \dots$ . The same reasoning holds true for the momentum-representation of the wave-function:

$$|\Psi(\mathbf{p}_1, \dots, \mathbf{p}_N)|^2 d\mathbf{p}_1 \dots d\mathbf{p}_N$$

is the probability of simultaneously finding a particle with momentum in the vicinity of  $\hbar^3 d\mathbf{p}_1$  while another particle has momentum in the vicinity of  $\hbar^3 d\mathbf{p}_2$  and so on.

It is useful to have a more general way to express the many-particle wave-function that is independent of representation. In quantum mechanics, we get to the position representation by taking the inner product of a *position eigenstate*  $|\mathbf{x}\rangle$  and a state vector  $|\psi\rangle$ . The wave function is  $\langle \mathbf{x} | \psi \rangle = \psi(\mathbf{x})$ . In the same sense, the many-body wave function with  $N$  particles is

$$\langle \mathbf{x}_1, \dots, \mathbf{x}_N | \Psi \rangle = \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$$

Okay. What does this tell us? Well the function  $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$  is a smooth but otherwise arbitrary function of  $3N$  variables. Its expansion in plane-waves can be written [32]

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_{\mathbf{k}_1, \dots, \mathbf{k}_N} a(\mathbf{k}_1, \dots, \mathbf{k}_N) \exp(i\mathbf{k}_1 \cdot \mathbf{x}_1 + \dots + i\mathbf{k}_N \cdot \mathbf{x}_N) \quad (54)$$

$a(\mathbf{k}_1, \dots, \mathbf{k}_N)$  is the expansion coefficient for a particular set of wave-vectors. Any normalization factors are stuck into  $a(\mathbf{k}_1, \dots, \mathbf{k}_N)$ . Plane-waves are momentum eigenstates  $\langle \mathbf{x} | \mathbf{k} \rangle \propto \exp(i\mathbf{k} \cdot \mathbf{x})$ . The wave-function eq. 54 can be rewritten as

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \langle \mathbf{x}_1, \dots, \mathbf{x}_N | \sum_{\mathbf{k}_1, \dots, \mathbf{k}_N} a(\mathbf{k}_1, \dots, \mathbf{k}_N) | \mathbf{k}_1, \dots, \mathbf{k}_N \rangle$$

<sup>16</sup> Actually only true in 3D. This is proved by the spin-statistics theorem in quantum field theory. More generally,  $\alpha = \exp(i\theta)$ . In 3D,  $\theta = 0, \pi$  for bosons and fermions respectively. It turns out that in 2D,  $\theta$  can be something else and those types of particles are called *anyons*.

The state  $|\mathbf{k}_1, \dots, \mathbf{k}_N\rangle \equiv |\mathbf{k}_1\rangle \otimes |\mathbf{k}_2\rangle \otimes \dots \otimes |\mathbf{k}_N\rangle$  is just the *tensor product* of all the single plane-wave states. The notation  $\otimes$  means tensor product. However, the symbol  $\otimes$  is a burden to typeset so let's drop it and just assume that when a product of states is written as  $|\psi\rangle|\phi\rangle \equiv |\psi\rangle \otimes |\phi\rangle \equiv |\psi, \phi\rangle$  the tensor product is implied. The position-matrix elements are

$$\langle \mathbf{x}_1, \dots, \mathbf{x}_N | \mathbf{k}_1, \dots, \mathbf{k}_N \rangle = \langle \mathbf{x}_1 | \mathbf{k}_1 \rangle \dots \langle \mathbf{x}_N | \mathbf{k}_N \rangle \equiv \psi_{\mathbf{k}_1}(\mathbf{x}_1) \dots \psi_{\mathbf{k}_N}(\mathbf{x}_N)$$

So then the many-body wave-function can be written as

$$\Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) = \sum_{\mathbf{k}_1, \dots, \mathbf{k}_N} a(\mathbf{k}_1, \dots, \mathbf{k}_N) \psi_{\mathbf{k}_1}(\mathbf{x}_1) \dots \psi_{\mathbf{k}_N}(\mathbf{x}_N)$$

This is an interesting way to write it. It is a (possibly infinite) sum of products of  $N$  single-particle wave-functions. We can readily convert this to momentum-representation. But we want to generalize to be independent of representation, so instead let's work with the ket  $|\Psi\rangle$

$$|\Psi\rangle = \sum_{\mathbf{k}_1 \dots \mathbf{k}_N} a(\mathbf{k}_1, \dots, \mathbf{k}_N) |\mathbf{k}_1\rangle \dots |\mathbf{k}_N\rangle$$

Just like in quantum mechanics, we are free to express the states  $|\mathbf{k}_i\rangle$  in a new basis. Let  $|\phi_\alpha\rangle$  be some other complete set of states. In the new basis  $|\mathbf{k}_i\rangle = \sum_\alpha \langle \phi_\alpha | \mathbf{k}_i \rangle |\phi_\alpha\rangle \equiv \sum_\alpha b(\alpha, \mathbf{k}_i) |\phi_\alpha\rangle$ . It is possible to rewrite the many-body wave-function as

$$|\Psi\rangle = \sum_{\alpha_1, \dots, \alpha_N} \left( \sum_{\mathbf{k}_1 \dots \mathbf{k}_N} a(\mathbf{k}_1, \dots, \mathbf{k}_N) b(\alpha_1, \mathbf{k}_1) \dots b(\alpha_N, \mathbf{k}_N) \right) |\phi_{\alpha_1}\rangle \dots |\phi_{\alpha_N}\rangle$$

The wave-vectors  $\mathbf{k}_i$  only show up in the sum in parenthesis. They are summed over (it's an ugly sum, but it's just a sum). Let's call it  $c(\alpha_1, \dots, \alpha_N)$ . Finally, it is obvious that the many-body wave-function can be written, in any basis, as

$$\begin{aligned} |\Psi\rangle &= \sum_{\alpha_1, \dots, \alpha_N} c(\alpha_1, \dots, \alpha_N) |\phi_{\alpha_1}\rangle \dots |\phi_{\alpha_N}\rangle \\ \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N) &= \sum_{\alpha_1, \dots, \alpha_N} c(\alpha_1, \dots, \alpha_N) \phi_{\alpha_1}(\mathbf{x}_1) \dots \phi_{\alpha_N}(\mathbf{x}_N) \end{aligned} \tag{55}$$

The wave-function for an interacting system of  $N$  particles can be written as a sum of products of  $N$  single-particle wave-functions. This is true in any basis and any representation (we saw e.g. position and momentum representations above). We could let  $\phi_\alpha(\mathbf{x})$  be, for instance, Hydrogen-like atomic orbitals. In this case,  $\alpha \equiv \{n, l, m\}$  is a composite index for more than one quantum number. For more technical mumbo-jumbo see §2.1.4 in Martin [51] where it is proved that tensor products of single-particle wave-functions form a complete basis in the  $N$  dimensional Hilbert space of  $N$  interacting particles. There are similar details in §2.1 in Altland and Simons [4].

Still, we know that eq. 55 has to satisfy symmetry or anti-symmetry with respect to particle exchange depending on the types of particles. This imposes constraints on the coefficients  $c(\alpha_1, \dots, \alpha_N)$ . We saw a special case of this earlier in eq. 20: the Slater determinant.

It turns out that, if the particles don't interact, there are only  $N$  orbitals to consider and the wave-function is just permutations of the same set of orbitals. The coefficients can only differ by a sign and the signs must be chosen to satisfy the (anti-)symmetry requirements. Slater determinants are eigenstates of non-interacting many-body Hamiltonians but not for interacting ones. Still, they form a basis and linear combinations of Slater determinants are eigenstates of interacting many-body Hamiltonians.

### 7.3 Occupation-Number Representation

This section follows §2.1.7 in Martin [51] and Chp. 2 in Altland and Simmon [4]. The occupation-number or just “number representation” (sometimes also called “Fock representation”) is more *defined* than derived. It can be arrived at formally for quantum harmonic oscillators (i.e. Bosons), but for many quantum systems (and for Fermions in general), the number representation is a rather abstract notation that is defined by the algebra of its operators. In many-body problems, it is just written down and understood by analogy. The state  $|n_1, n_2, \dots\rangle$  is “the state with  $n_\alpha$  particles occupying the  $\alpha^{th}$  single-particle level with energy  $\epsilon_\alpha$ .” The labels  $\alpha$  are not particle labels but are instead the quantum numbers of the basis. For example, consider the momentum representation encountered earlier. In the number representation, the labels  $\alpha$  denote the momentum  $\mathbf{k}_1$ .

Let's figure out how to write a wave-function in the number representation. For non-interacting Fermions, a Slater determinant of plane-waves is an eigenstate. Let's do 2 particles in 1D and pick an eigenstate wave-function involving the momenta  $k$  and  $p$ . The Hamiltonian is

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m_e} \left[ \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right]$$

and the wave-function is

$$\Psi_{k,p}(x_1, x_2) = (2)^{-1/2} [\psi_k(x_1)\psi_p(x_2) - \psi_k(x_2)\psi_p(x_1)]$$

The plane-waves are normalized  $\psi_k(x) = (L)^{-1/2} \exp(ikx)$  in a 1D box with “volume”  $L$ . First, note that  $\Psi_{p,p}(x, x) = \Psi_{k,k}(x_1, x_2) = 0$ . Both of these facts are a consequence of the Pauli exclusion principle that is encoded by the anti-symmetry requirement on the wave-function. From now on, assume  $k \neq p$ . The energy expectation value is

$$\mathcal{E} = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle = \frac{\hbar^2 k^2}{2m_e} + \frac{\hbar^2 p^2}{2m_e}$$

Our goal is to compute the energy expectation value above in the number representation. From our discussion above, the number state is

$$|n\rangle \equiv |n_k, n_p, \dots, n_q, \dots\rangle = |1, 1, 0, \dots, 0, \dots\rangle$$

The eigenvalues are  $\epsilon_k = \hbar^2 k^2 / (2m_e)$  and  $\epsilon_p = \hbar^2 p^2 / (2m_e)$ . Thus we see that the expectation value can be written

$$\mathcal{E} = \langle n | \hat{\mathcal{H}} | n \rangle \equiv \sum_{\alpha} \langle n | \hat{n}_{k_{\alpha}} | n \rangle \epsilon_{k_{\alpha}} = \sum_{\alpha} n_{k_{\alpha}} \epsilon_{k_{\alpha}} = n_k \epsilon_k + n_p \epsilon_p \quad (56)$$

with  $n_k = n_p = 1$ . We define the number operator as  $\hat{n}_\alpha \equiv \hat{c}_\alpha^\dagger \hat{c}_\alpha$  where  $\hat{c}_\alpha^\dagger$  and  $\hat{c}_\alpha$  are the creation and annihilation operators respectively. They are qualitatively different objects depending on whether the particles are Fermions or Bosons. In the case of *non*-interacting free particles  $\epsilon_{k_\alpha}$  is just the kinetic energy of a particle with momentum  $\hbar k$ . However, eq. 56 holds more generally. Even for interacting particles, we can write the Hamiltonian in the number representation and it will look like eq. 56.

The creation operator is defined by its action on a number state<sup>17,18</sup>:

$$\hat{c}_\alpha^\dagger |n_1, \dots, n_\alpha, \dots\rangle \equiv (n_\alpha + 1)^{1/2} |n_1, \dots, n_\alpha + 1, \dots\rangle$$

that is, the creation operator “creates” a particle in the  $\alpha^{th}$  state. The prefactor is for normalization. The usefulness of this operator is that, by repeated application of the creation operator, we can create *any* arbitrary state of the system

$$|n_1, \dots, n_\alpha, \dots\rangle = \left( \prod_i \frac{(\hat{c}_i)^{n_i}}{(n_i!)^{1/2}} \right) |0\rangle$$

The state  $|0\rangle$  is the “vacuum state,” i.e. the state with no particles present. Taking the Hermitian conjugate of the creation operators, we also have

$$\hat{c}_\alpha |n_1, \dots, n_\alpha, \dots\rangle \equiv (n_\alpha)^{1/2} |n_1, \dots, n_\alpha - 1, \dots\rangle$$

i.e.  $\hat{c}_\alpha$  annihilates a particle from the  $\alpha^{th}$  state. The requirement of (anti-)symmetry of the (Fermion) Boson wave function implies a lot about these operators. Let us see why.

### 7.3.1 Fermions

Assume we are working with a state with only two particles in it: one in the  $\alpha^{th}$  state and one in the  $\beta^{th}$  state (assume  $\alpha \neq \beta$ ). There are two ways to create this state; (i) put a particle in the  $\alpha^{th}$  state first, then one in the  $\beta^{th}$  state. (ii) put a particle in the  $\beta^{th}$  state first, then one in the  $\alpha^{th}$  state. This is equivalent to “swapping” the particles. If they are Fermions, this means that the wave function has to change sign; i.e.

$$\begin{aligned} \hat{c}_\beta^\dagger \hat{c}_\alpha^\dagger |0\rangle &= -\hat{c}_\alpha^\dagger \hat{c}_\beta^\dagger |0\rangle \\ (\hat{c}_\beta^\dagger \hat{c}_\alpha^\dagger + \hat{c}_\alpha^\dagger \hat{c}_\beta^\dagger) |0\rangle &= 0 \end{aligned}$$

The  $\hat{A}\hat{B} + \hat{B}\hat{A}$  thing looks a lot like a commutator, except there is a  $+$  sign. It is called an “anticommutator” and is usually written  $\{\hat{A}, \hat{B}\}$ . For the  $\alpha = \beta$  case, recall that it is

<sup>17</sup> These aren’t just some random operators we made up; they are a unique and perfectly equivalent representation of our many-body Hilbert space. The *Stone-von Neumann* theorem proves this.

<sup>18</sup> See the derivation in Altland and Simons and here [2]. This equation, as written, doesn’t agree with those refs. There is supposed to be a  $\pm$  phase depending on how many particles there are in other states... something to do with enforcing anti-symmetry. Oh well. It doesn’t affect results further down. I think, conceptually, the phase is due to the fact that the overall sign of the state depends on the order in which it is created. i.e. if we put a particle in state 1 first and then in state 2, as opposed to in state 2 first then state 1, we have equivalently “swapped” the particles between the two wave functions and they have to differ by a sign. Then again, the definition below is perfectly consistent with what is in Ziman [86]

necessary that the Fermion wave function vanish if we put two particles in the same state: i.e.

$$\hat{c}_\alpha^\dagger \hat{c}_\alpha^\dagger + \hat{c}_\alpha \hat{c}_\alpha = 0$$

which is only satisfied if  $(\hat{c}_\alpha^\dagger)^2 = 0$ . So for the Fermion creation operators, we conclude

$$\{\hat{c}_\alpha^\dagger, \hat{c}_\beta^\dagger\} = 0 \quad \forall \alpha, \beta$$

We can also show

$$\{\hat{c}_\alpha, \hat{c}_\beta\} = 0 \quad \forall \alpha, \beta$$

What remains is the case  $\{\hat{c}_\alpha, \hat{c}_\beta^\dagger\}$ . To see what happens, consider first  $\alpha \neq \beta$ . Since we can't annihilate the vacuum state (i.e.  $\hat{c}_\alpha|0\rangle \equiv 0 \quad \forall \alpha$ ) we have

$$\begin{aligned} \hat{c}_\alpha^\dagger \hat{c}_\beta |0\rangle &= 0 \\ \hat{c}_\alpha \hat{c}_\beta^\dagger |0\rangle &= 0 \end{aligned}$$

Then it is true that

$$(\hat{c}_\alpha^\dagger \hat{c}_\beta + \hat{c}_\alpha \hat{c}_\beta^\dagger) |0\rangle = 0$$

i.e.  $\{\hat{c}_\alpha, \hat{c}_\beta^\dagger\} = 0 \quad \forall \alpha \neq \beta$ . Finally, let us consider  $\alpha \equiv \beta$ . Note that the following operations have to be true

$$\begin{aligned} \hat{c}_\alpha^\dagger \hat{c}_\alpha |0\rangle &= 0 & \hat{c}_\alpha \hat{c}_\alpha^\dagger |0\rangle &= |0\rangle \\ \hat{c}_\alpha^\dagger \hat{c}_\alpha |1_\alpha\rangle &= |1_\alpha\rangle & \hat{c}_\alpha \hat{c}_\alpha^\dagger |1_\alpha\rangle &= 0 \end{aligned}$$

Add all of these together to find

$$(\hat{c}_\alpha \hat{c}_\alpha^\dagger + \hat{c}_\alpha^\dagger \hat{c}_\alpha) |0\rangle + (\hat{c}_\alpha \hat{c}_\alpha^\dagger + \hat{c}_\alpha^\dagger \hat{c}_\alpha) |1_\alpha\rangle = |0\rangle + |1_\alpha\rangle$$

By orthogonality of the states, we find  $\{\hat{c}_\alpha, \hat{c}_\alpha^\dagger\} = 1$ . To summarize this section, the Fermion operators obey the anticommutation relations ( $\forall \alpha, \beta$ )

$$\begin{aligned} \{\hat{c}_\alpha, \hat{c}_\beta\} &= 0 \\ \{\hat{c}_\alpha^\dagger, \hat{c}_\beta^\dagger\} &= 0 \\ \{\hat{c}_\alpha, \hat{c}_\beta^\dagger\} &= \delta_{\alpha\beta} \end{aligned} \tag{57}$$

A final note: since Fermion operators must obey the above anticommutation relations, it turns out that the number operator  $\hat{n} \equiv \hat{c}^\dagger \hat{c}$  satisfies  $\hat{n}^2 = \hat{n} \hat{n}$ . The state-index is suppressed for convenience. That this is true follows from

$$\hat{n} \hat{n} |n\rangle = \hat{c}^\dagger \hat{c} \hat{c}^\dagger \hat{c} |n\rangle = \hat{c}^\dagger (1 - \hat{c}^\dagger \hat{c}) \hat{c} |n\rangle = \hat{c}^\dagger \hat{c} |n\rangle - \underbrace{\hat{c}^\dagger \hat{c}^\dagger \hat{c} \hat{c} |n\rangle}_{\equiv 0} = \hat{n} |n\rangle$$

where the term which annihilates the state twice vanishes due to the Pauli principle ( $0 \leq n \leq 1$ ).

### 7.3.2 Bosons

The treatment of Bosons is available in many places: in particular, see §1 of Ziman [86]. The derivation is probably familiar to most people in field, so let's omit it. The qualitative difference from Fermions is that the Boson wave function is *symmetric* which implies that any number of particles can occupy the same state. The same reasoning as in the last section leads to ( $[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$  is the *commutator*):

$$\begin{aligned} [\hat{a}_\alpha, \hat{a}_\beta] &= 0 \\ [\hat{a}_\alpha^\dagger, \hat{a}_\beta^\dagger] &= 0 \\ [\hat{a}_\alpha, \hat{a}_\beta^\dagger] &= \delta_{\alpha\beta} \end{aligned} \tag{58}$$

$\forall \alpha, \beta$ . From now on, we will occasionally use  $\hat{a}$  for Bosons and  $\hat{c}$  for Fermions but usually the context will make it clear what kinds of particles we are studying.

## 7.4 Field Operators

This section follows Gurarie's notes [32] and Altland and Simons §2.1 [4]. In §7.3, we encountered the creation and annihilation operators. When talking about Fermions, we used  $\hat{c}$  etc. but we will talk about Bosons for now and it is customary to use  $\hat{a}$  etc. Moreover, we will be working with a plane-wave basis so it is reasonable to label the operators by the momentum eigenstate they act on: e.g.  $\hat{a}_{\mathbf{k}}^\dagger$  and  $\hat{a}_{\mathbf{k}}$  are creation and annihilation operators on the  $\mathbf{k}$  momentum eigenstate. For many purposes, it will be convenient to have a formulation in real space too. Earlier, we implicitly used the fact that we can represent the many-body wave function in any basis. Let us explicitly show it now. First of all, recall that, for a complete basis  $|\alpha\rangle$ , we can write the identity operator as

$$\hat{1} = \sum_{\alpha} |\alpha\rangle\langle\alpha|$$

With this, we can rewrite an arbitrary state,  $|\beta\rangle$ , as

$$|\beta\rangle = \hat{a}_\beta^\dagger |0\rangle = \sum_{\alpha} |\alpha\rangle\langle\alpha|\beta\rangle = \sum_{\alpha} \langle\alpha|\beta\rangle \hat{a}_\alpha^\dagger |0\rangle$$

where we identify

$$\hat{a}_\beta^\dagger = \sum_{\alpha} \langle\alpha|\beta\rangle \hat{a}_\alpha^\dagger \tag{59}$$

The obvious continuum generalization, which we will need to go to position space, is

$$\hat{a}^\dagger(\beta) = \int d\alpha \langle\alpha|\beta\rangle \hat{a}^\dagger(\alpha)$$

Note that the basis transformation for the annihilation operator can be obtained by taking the Hermitian conjugate of eq. 59.

So it's clear that we are free to represent these operators in any complete basis. The *field operators* (“field” means their domain is continuous) in the position representation are defined as

$$\begin{aligned}\hat{\psi}(\mathbf{x}) &= V^{-1/2} \sum_{\mathbf{k}} \hat{a}_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{x}) \\ \hat{\psi}^\dagger(\mathbf{x}) &= V^{-1/2} \sum_{\mathbf{k}} \hat{a}_{\mathbf{k}}^\dagger \exp(-i\mathbf{k} \cdot \mathbf{x})\end{aligned}\tag{60}$$

They are Fourier transforms of operators that create (annihilate) particles with particular momenta so their physical interpretation is that they create or annihilate a particle *at the point*  $\mathbf{x}$ . Their commutation relation can be derived from the momentum space creation and annihilation operators:  $[\hat{\psi}(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{y})] = \delta(\mathbf{x} - \mathbf{y})$ . Note that the inverse Fourier transforms of the field operators are

$$\begin{aligned}\hat{a}_{\mathbf{k}} &= V^{-1/2} \int d\mathbf{x} \hat{\psi}(\mathbf{x}) \exp(-i\mathbf{k} \cdot \mathbf{x}) \\ \hat{a}_{\mathbf{k}}^\dagger &= V^{-1/2} \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \exp(i\mathbf{k} \cdot \mathbf{x})\end{aligned}$$

The normalization by  $V^{-1/2}$  is so that  $\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})$  can be interpreted as the density of particles. Indeed

$$\int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x}) = V^{-1} \sum_{\mathbf{k}, \mathbf{k}'} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}'} \int d\mathbf{x} \exp(i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{x}) = \sum_{\mathbf{k}} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}}\tag{61}$$

will give us the total number of particles.  $\hat{n}_{\mathbf{k}} = \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}}$  is a *number operator*; it counts the number of particles with momentum  $\mathbf{k}$ .

Our next step is to learn how to express the Hamiltonian in terms of these operators. We will only consider one- and two-particle operators; operators involving more than two particles at once are rare and infrequently studied. Let us do one-particle operators first.

### 7.4.1 One-Body Operators

In general, a one-body operator in a Hamiltonian looks like

$$\hat{O}_1 = \sum_i^N \hat{o}_i$$

where  $\hat{o}_i$  is a one-particle operator. The sum runs over all particles. We proceed by picking a basis in which operators  $\hat{o}$  are diagonal and evaluating the expectation value there. Let the eigenvectors of  $\hat{o}$  be  $|\alpha\rangle$ . We use the completeness relations again

$$\begin{aligned}\hat{o} &= \sum_{\alpha, \alpha'} |\alpha\rangle \langle \alpha| \hat{o} |\alpha'\rangle \langle \alpha'| = \sum_{\alpha, \alpha'} \langle \alpha| \hat{o} |\alpha'\rangle |\alpha\rangle \langle \alpha'| = \sum_{\alpha} |\alpha\rangle o_{\alpha} \langle \alpha| \\ o_{\alpha} &= \langle \alpha| \hat{o} |\alpha\rangle\end{aligned}$$



The second line follows from the assumption that this is the diagonal basis. Now notice that

$$\hat{O}_1 = \sum_i \hat{o}_i = \sum_i \sum_{\alpha} |\alpha\rangle o_{\alpha} \langle\alpha| \equiv \sum_{\alpha} o_{\alpha} n_{\alpha} |\alpha\rangle \langle\alpha|$$

where the sum over  $i$  counts 1 for each operator with matrix element  $o_{\alpha}$ . We don't have to care which particles are in the state because they are indistinguishable (i.e. we can drop the  $i$  label). The factor  $n_{\alpha}$  is how many particles have the eigenvalue  $\alpha$ . Based on the appearance of the  $n_{\alpha}$  factor in the operator above, we postulate that, in second quantization, it can be rewritten

$$\hat{O}_1 = \sum_i \hat{o}_i = \sum_{\alpha} o_{\alpha} \hat{n}_{\alpha} = \sum_{\alpha} o_{\alpha} \hat{a}_{\alpha}^{\dagger} \hat{a}_{\alpha} \quad (62)$$

That this is the correct way to write it can be verified by calculating the matrix element of  $\hat{O}$  in both the number representation and by e.g. Slater determinants. The equivalence of the result in both cases proves eq. 62 [2, 4]. If we want to write a one-body operator in an arbitrary representation, i.e. not necessarily one in which it is diagonal, we can use eq. 59.

$$\begin{aligned} \hat{O}_1 &= \sum_{\alpha} o_{\alpha} \hat{a}_{\alpha}^{\dagger} \hat{a}_{\alpha} = \sum_{\beta\beta'} \langle\beta| \overbrace{\left( \sum_{\alpha} |\alpha\rangle o_{\alpha} \langle\alpha| \right)}^{\hat{O}} |\beta'\rangle \hat{a}_{\beta}^{\dagger} \hat{a}_{\beta'} \\ &= \sum_{\beta\beta'} \langle\beta|\hat{O}|\beta'\rangle \hat{a}_{\beta}^{\dagger} \hat{a}_{\beta'} \end{aligned} \quad (63)$$

As an example, let's do the kinetic energy operator! The kinetic energy operator on a system of electrons is diagonal in the momentum (or *crystal* momentum) basis. Let  $\mathbf{k}$  be the momentum (well,  $\hbar\mathbf{k}$  but we don't care about the distinction). The matrix element is  $\langle\mathbf{k}|\hat{p}^2|\mathbf{k}\rangle = \hbar^2 k^2$ . Then

$$\hat{T} = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m_e} \hat{a}_{\mathbf{k}}^{\dagger} \hat{a}_{\mathbf{k}}$$

In a similar way, since (local) potentials are diagonal in position space, we can write

$$\hat{V} = \int d\mathbf{x} V(\mathbf{x}) \hat{\psi}^{\dagger}(\mathbf{x}) \hat{\psi}(\mathbf{x}) \quad (64)$$

The *physical* interpretation is that the potential couples to the density of particles at the point  $\mathbf{x}$ ,  $\hat{\psi}^{\dagger}(\mathbf{x}) \hat{\psi}(\mathbf{x}) \equiv \hat{\rho}(\mathbf{x})$ . That this is an operator is due to the fact that we don't know what the density is yet; once we know the ground-state wave function, we can calculate the expectation value which tells us the energy. E.g., if  $V(\mathbf{x})$  is an electrostatic potential, the expectation value of eq. 64 tells us the electrostatic energy of our system.

Later on, we will want both the kinetic energy in position space and the potential in reciprocal space, so let's work those out now too. Let's do the kinetic energy first.

$$\hat{T} = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m_e} \hat{a}_{\mathbf{k}}^{\dagger} \hat{a}_{\mathbf{k}} = \frac{\hbar^2}{2m_e} \sum_{\mathbf{k}, \mathbf{k}'} \mathbf{k} \cdot \mathbf{k}' \hat{a}_{\mathbf{k}}^{\dagger} \hat{a}_{\mathbf{k}'} \delta_{\mathbf{k}, \mathbf{k}'}$$

Recall that we can write  $\delta_{\mathbf{k},\mathbf{k}'} = V^{-1} \int d\mathbf{x} \exp(-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{x})$ . Then

$$\begin{aligned} \hat{T} &= \frac{\hbar^2}{V 2m_e} \int d\mathbf{x} \left( \sum_{\mathbf{k}} \hat{a}_{\mathbf{k}}^\dagger \mathbf{k} \exp(-i\mathbf{k} \cdot \mathbf{x}) \right) \cdot \left( \sum_{\mathbf{k}'} \hat{a}_{\mathbf{k}'} \mathbf{k}' \exp(i\mathbf{k}' \cdot \mathbf{x}) \right) = \\ &= \frac{\hbar^2}{2m_e} \int d\mathbf{x} \frac{\partial}{\partial \mathbf{x}} \left( V^{-1/2} \sum_{\mathbf{k}} \hat{a}_{\mathbf{k}}^\dagger \exp(-i\mathbf{k} \cdot \mathbf{x}) \right) \cdot \frac{\partial}{\partial \mathbf{x}} \left( V^{-1/2} \sum_{\mathbf{k}'} \hat{a}_{\mathbf{k}'} \exp(i\mathbf{k}' \cdot \mathbf{x}) \right) \\ &= \frac{\hbar^2}{2m_e} \int d\mathbf{x} \frac{\partial \hat{\psi}^\dagger}{\partial \mathbf{x}} \cdot \frac{\partial \hat{\psi}}{\partial \mathbf{x}} \end{aligned}$$

It will be convenient to also have this in another equivalent real space notation:

$$\frac{\hbar^2}{2m_e} \int d\mathbf{x} \frac{\partial \hat{\psi}^\dagger}{\partial \mathbf{x}} \cdot \frac{\partial \hat{\psi}}{\partial \mathbf{x}} = -\frac{\hbar^2}{2m_e} \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \left( \frac{\partial^2}{\partial \mathbf{x}^2} \right) \hat{\psi}(\mathbf{x}) = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \frac{\hat{\mathbf{p}}^2}{2m_e} \hat{\psi}(\mathbf{x})$$

which can be proved using integration by parts and noting that the boundary term vanishes (we could use either  $\hat{\psi} \rightarrow 0$  vanishes on the boundary or  $\hat{\psi} \rightarrow \hat{\psi}$ , i.e. PBC). The potential energy is much easier to do.

$$\begin{aligned} \hat{V} &= \int d\mathbf{x} V(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) = V^{-1} \sum_{\mathbf{k},\mathbf{k}'} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}'} \int d\mathbf{x} V(\mathbf{x}) \exp(-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{x}) \\ &= \sum_{\mathbf{k},\mathbf{k}'} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} \end{aligned}$$

where  $V_{\mathbf{k}-\mathbf{k}'}$  is the Fourier transform of the potential (see eq. 41). Then, to summarize, the kinetic energy operator in both representations is

$$\hat{T} = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m_e} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}} = \frac{\hbar^2}{2m_e} \int d\mathbf{x} \frac{\partial \hat{\psi}^\dagger}{\partial \mathbf{x}} \cdot \frac{\partial \hat{\psi}}{\partial \mathbf{x}} = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \frac{\hat{\mathbf{p}}^2}{2m_e} \hat{\psi}(\mathbf{x}) \quad (65)$$

and the potential in both representations is

$$\hat{V} = \int d\mathbf{x} V(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) = \sum_{\mathbf{k},\mathbf{k}'} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} \quad (66)$$

#### 7.4.2 Two-Body Operators

The formal development of two body operators in second quantization is skimmed over in Altland and Simons [4], another ref. [2], and even in Ziman [86]. So I will skim over it too. Let's just write down the result. Suppose we have a potential that acts on each particle's coordinate simultaneously; then

$$\hat{U} = \int d\mathbf{x} d\mathbf{x}' U(\mathbf{x}, \mathbf{x}') \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \hat{\psi}(\mathbf{x}')$$

Physically, this represents particles at  $\mathbf{x}$  and  $\mathbf{x}'$  interacting; the “size” of the interaction is proportional to the density of particles at each point. We should include a factor of 1/2 in

front of this because each integral counts the same interaction once, so it's counted twice... but I don't want to carry it around, so I will omit until later. The meaning of this expression is a little more transparent in Fourier space. The Fourier transform is

$$\begin{aligned}\hat{U} &= V^{-2} \sum_{\mathbf{k}\mathbf{k}'\mathbf{p}\mathbf{p}'} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{k}'} \hat{a}_{\mathbf{p}'} \int d\mathbf{x} d\mathbf{x}' U(\mathbf{x}, \mathbf{x}') \exp(-i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{x}) \exp(-i(\mathbf{p} - \mathbf{p}') \cdot \mathbf{x}') \\ &= \sum_{\mathbf{k}\mathbf{k}'\mathbf{p}\mathbf{p}'} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{k}'} \hat{a}_{\mathbf{p}'} U_{\mathbf{k}-\mathbf{k}'; \mathbf{p}-\mathbf{p}'}\end{aligned}$$

This term means a particle in the state  $\mathbf{p}$  scatters off another particle in the state  $\mathbf{p}'$ ; after scattering, they are injected into the states  $\mathbf{k}$  and  $\mathbf{k}'$ . The probability of scattering is  $U_{\mathbf{k}-\mathbf{k}'; \mathbf{p}-\mathbf{p}'}$ .

Note the particular way the operators are ordered. Such a way of ordering them is called *normal ordering*: this means all  $\dagger$ 's are on the left. An alternative and, at a glance, sensible way of writing the interaction would be

$$\begin{aligned}\hat{U} &= \int d\mathbf{x} d\mathbf{x}' U(\mathbf{x}, \mathbf{x}') \hat{\rho}(\mathbf{x}) \hat{\rho}(\mathbf{x}') = \int d\mathbf{x} d\mathbf{x}' U(\mathbf{x}, \mathbf{x}') \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}') \\ &= \sum_{\mathbf{k}\mathbf{k}'\mathbf{p}\mathbf{p}'} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}'} \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}'} U_{\mathbf{k}-\mathbf{k}'; \mathbf{p}-\mathbf{p}'}\end{aligned}$$

Why is this not the preferred expression (§1.2 in ref. [50])? Suppose we have a state  $\hat{a}_\alpha^\dagger |0\rangle$  that contains one particle in the state  $\alpha$ . In the normal ordered expression,

$$\hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{k}'} \hat{a}_{\mathbf{p}'} (\hat{a}_\alpha^\dagger |0\rangle) = 0$$

since, even in the case that  $\alpha \equiv \mathbf{p}'$ , the next annihilation operator acts on the vacuum and  $\hat{a}_{\mathbf{k}'}^\dagger |0\rangle = 0$ . This is a sensible result since there are no two-particle interactions in a state with only one particle! On the other hand, if we let the other expression act on the  $\alpha$  state, we get

$$\hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}'} \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}'} (\hat{a}_\alpha^\dagger |0\rangle) = \delta_{\alpha\mathbf{p}'} \delta_{\mathbf{p}\mathbf{k}'} (\hat{a}_{\mathbf{k}}^\dagger |0\rangle)$$

There are cases where the two-particle interaction is not zero; in particular, this term is non-vanishing *for a particle interacting with itself!*

Note that, using the (anti-)commutation relations, we can convert to the normal ordered representation.

$$\begin{aligned}\hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}') &= \hat{\psi}^\dagger(\mathbf{x}) [\delta(\mathbf{x} - \mathbf{x}') \pm \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x})] \hat{\psi}(\mathbf{x}') \\ &= \delta(\mathbf{x} - \mathbf{x}') \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}') \pm \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \hat{\psi}(\mathbf{x}')\end{aligned}$$

Then

$$\begin{aligned}\hat{U} &= \int d\mathbf{x} d\mathbf{x}' U(\mathbf{x} - \mathbf{x}') \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}') \\ &= \int d\mathbf{x} d\mathbf{x}' U(\mathbf{x}, \mathbf{x}') \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \hat{\psi}(\mathbf{x}') \pm \int d\mathbf{x} U(\mathbf{x}, \mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x})\end{aligned}$$

For  $U(\mathbf{x}, \mathbf{x}') \sim |\mathbf{x} - \mathbf{x}'|^{-1}$  the Coulomb potential, the last term diverges! i.e. we should use the normal ordered version to avoid this term. Still, the Coulomb potential is translationally invariant and the potential operator becomes

$$\hat{U} = \int d\mathbf{x} d\mathbf{x}' U(\mathbf{x}, \mathbf{x}') \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \hat{\psi}(\mathbf{x}') \pm U(0) \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x})$$

The last integral is just the particle number operator,  $\hat{N}$ , so that this last term is effectively just an unobservable constant that we can dispose of by, e.g. jamming it into the definition of the chemical potential. Rather than deal with this, we ought to just resolve to work with normal ordered two-body operators.

So, to conclude this section, we can write two body operators in either real or reciprocal space as

$$\hat{U} = \int d\mathbf{x} d\mathbf{x}' U(\mathbf{x}, \mathbf{x}') \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \hat{\psi}(\mathbf{x}') = \sum_{\mathbf{k}\mathbf{k}'\mathbf{p}\mathbf{p}'} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{k}'} \hat{a}_{\mathbf{p}'} U_{\mathbf{k}-\mathbf{k}'; \mathbf{p}-\mathbf{p}'} \quad (67)$$

### 7.4.3 Second Quantized Hamiltonians

It is theoretically inconvenient (and experimentally impossible in condensed matter) to fix the particle number  $N$ . Instead, it is easier to work in the *Grand-Canonical* ensemble where chemical potential,  $\mu$ , is fixed. This can be achieved by adding a term

$$\begin{aligned} -\mu \hat{N} &= -\mu \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) \\ &= -\mu \sum_{\mathbf{k}} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}} \end{aligned}$$

Let us think about what this term “does.” Suppose the energy is minimized at some chemical potential energy  $U_0 = -\langle \Psi | \mu \hat{N} | \Psi \rangle = -\mu N$ . For *large* chemical potential, a small number of particles  $N$  achieves this value. On the other hand, for a *small* chemical potential, a large number of particles  $N$  is what we need. So then, just like in thermodynamics, the chemical potential controls the particle number with a large chemical potential leading to a small number of particles and vice versa. Note that, in the particular case  $\mu \equiv 0$ ,  $N$  can be anything. This is what happens with, e.g. phonons or photons.

Now let us put everything together and, once and for all, write down the second quantized version of the Hamiltonians we will work with. In the real space version, we have

$$\boxed{\begin{aligned} \hat{H} &= \frac{\hbar^2}{2m_e} \int d\mathbf{x} \frac{\partial \hat{\psi}^\dagger}{\partial \mathbf{x}} \cdot \frac{\partial \hat{\psi}}{\partial \mathbf{x}} - \mu \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) + \int d\mathbf{x} V(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) \\ &\quad + \int d\mathbf{x} d\mathbf{x}' U(\mathbf{x}, \mathbf{x}') \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \hat{\psi}(\mathbf{x}') \end{aligned}} \quad (68)$$

An alternative and, often times convenient, way to rewrite this is

$$\hat{H} = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \left[ \frac{\hat{\mathbf{p}}^2}{2m_e} - \mu + V(\mathbf{x}) \right] \hat{\psi}(\mathbf{x}) + \int d\mathbf{x} d\mathbf{x}' U(\mathbf{x}, \mathbf{x}') \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}) \hat{\psi}(\mathbf{x}') \quad (69)$$

We will very often want to work in momentum space. In that case, we have

$$\hat{H} = \sum_{\mathbf{k}\mathbf{k}'} \hat{a}_{\mathbf{k}}^\dagger \left[ \left( \frac{\hbar^2 \mathbf{k}^2}{2m_e} - \mu \right) \delta_{\mathbf{k}\mathbf{k}'} + V_{\mathbf{k}-\mathbf{k}'} \right] \hat{a}_{\mathbf{k}'} + \sum_{\mathbf{k}\mathbf{k}'\mathbf{p}\mathbf{p}'} \hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{k}'} \hat{a}_{\mathbf{p}'} U_{\mathbf{k}-\mathbf{k}';\mathbf{p}-\mathbf{p}'} \quad (70)$$

These are worth remembering!

## 7.5 Tight-Binding in the Second Quantization

“Tight-binding” offers a natural way to study interaction in systems with highly localized particles: e.g. insulators, Mott-Hubbard systems, etc. Moreover, the formalism is exact in second-quantization, atleast until we begin to neglect certain hopping or interaction terms.

### 7.5.1 One-Body Hamiltonian

See ref. [54]. To start, let us temporarily only consider a one-body Hamiltonian

$$\hat{H} = \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \left[ \frac{\hat{\mathbf{p}}^2}{2m_e} - \mu + V(\mathbf{x}) \right] \hat{\psi}(\mathbf{x}) \equiv \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \hat{h}(\mathbf{x}) \hat{\psi}(\mathbf{x})$$

with  $\hat{h}(\mathbf{x})$  the one-body Hamiltonian density. We assume that  $\hat{h}(\mathbf{x})$  and  $\hat{\psi}(\mathbf{x})$ ,  $\hat{\psi}^\dagger(\mathbf{x})$  are unit-cell periodic. These could be spinful particles, but we suppress the spin index for now. The derivation is the same with and without spin. We let

$$\begin{aligned} \hat{\psi}(\mathbf{x}) &= \sum_{\mathbf{R}\mu} \hat{c}_{\mathbf{R}\mu} w_{\mathbf{R}\mu}(\mathbf{x}) \\ \hat{\psi}^\dagger(\mathbf{x}) &= \sum_{\mathbf{R}\mu} \hat{c}_{\mathbf{R}\mu}^\dagger w_{\mathbf{R}\mu}^*(\mathbf{x}) \end{aligned} \quad (71)$$

with  $\mu$  represents a generalized band-index (in this case, it is a “site” at position  $\boldsymbol{\tau}_\mu$  in the unitcell at  $\mathbf{R}$ ) and  $i$  is the unitcell index. The functions  $w_{\mathbf{R}\mu}(\mathbf{x}) \equiv w_\mu(\mathbf{x} - (\mathbf{R} + \boldsymbol{\tau}_\mu))$  are supposed to form a complete set; they are called “Wannier functions”. Wannier functions are defined by<sup>19</sup>

$$\begin{aligned} |\psi_{\mathbf{R}n}\rangle &= N^{-1/2} \sum_{\mathbf{k}} \exp(-i\mathbf{k} \cdot \mathbf{R}) |\psi_{\mathbf{k}n}\rangle \\ w_{\mathbf{R}n}(\mathbf{x}) &\equiv \langle \mathbf{x} | \psi_{\mathbf{R}n} \rangle = N^{-1/2} \sum_{\mathbf{k}} \exp(-i\mathbf{k} \cdot \mathbf{R}) \psi_{\mathbf{k}n}(\mathbf{x}) \end{aligned}$$

where  $|\psi_{\mathbf{k}n}\rangle$  is a Bloch function. Obviously the Wannier functions are periodic with respect to translation by a lattice vector. The Wannier states form a complete, orthonormal set:

$$\begin{aligned} \langle \psi_{\mathbf{R}'n'} | \psi_{\mathbf{R}n} \rangle &= N^{-1} \sum_{\mathbf{k}\mathbf{k}'} \exp(-i\mathbf{k} \cdot \mathbf{R} + i\mathbf{k}' \cdot \mathbf{R}') \langle \psi_{\mathbf{k}'n'} | \psi_{\mathbf{k}n} \rangle \\ N^{-1} \sum_{\mathbf{k}\mathbf{k}'} \exp(-i\mathbf{k} \cdot \mathbf{R} + i\mathbf{k}' \cdot \mathbf{R}') \delta_{\mathbf{k}\mathbf{k}'} \delta_{nn'} &= \frac{\delta_{nn'}}{N} \sum_{\mathbf{k}} \exp(-i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')) = \delta_{nn'} \delta_{\mathbf{R}\mathbf{R}'} \end{aligned}$$

<sup>19</sup> This is really only true for a set of mutually isolated bands; more generally, if the bands cross, the Wannier states are actually a linear combination of all bands of interest at each  $\mathbf{k}$ -point. This won’t matter in what follows though.

Completeness follows from

$$\langle \psi_{\mathbf{R}'n'} | \left( \sum_{\mathbf{R}n} |\psi_{\mathbf{R}n}\rangle \langle \psi_{\mathbf{R}n}| \right) | \psi_{\mathbf{R}''n''} \rangle = \delta_{\mathbf{R}'\mathbf{R}''} \delta_{n'n''}$$

i.e.  $\sum_{\mathbf{R}n} |\psi_{\mathbf{R}n}\rangle \langle \psi_{\mathbf{R}n}|$  is the identity matrix. The Wannier functions  $w_{\mathbf{R}\mu}(\mathbf{x})$  are defined by the unitary transformation

$$|\mathbf{x}\rangle = \sum_{\mathbf{R}\mu} |\psi_{\mathbf{R}\mu}\rangle \langle \psi_{\mathbf{R}\mu} | \mathbf{x} \rangle \equiv \sum_{\mathbf{R}\mu} w_{\mathbf{R}\mu}^*(\mathbf{x}) |\psi_{\mathbf{R}\mu}\rangle$$

We relate this to the definition eq. 71 by noting that a state with a particle at position  $\mathbf{x}$  can be written as  $|\mathbf{x}\rangle = \hat{\psi}^\dagger(\mathbf{x})|0\rangle$  (ignoring issues of convergence...). From this, combined with the equation above, we can deduce that

$$\hat{\psi}^\dagger(\mathbf{x}) = \sum_{\mathbf{R}\mu} w_{\mathbf{R}\mu}^*(\mathbf{x}) \hat{c}_{\mathbf{R}\mu}^\dagger$$

where  $\hat{c}_{\mathbf{R}\mu}^\dagger$  creates a particle at position  $\boldsymbol{\tau}_\mu$  in the unitcell at  $\mathbf{R}$ .

Then the one-body Hamiltonian becomes

$$\begin{aligned} \hat{H} &= \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \hat{h}(\mathbf{x}) \hat{\psi}(\mathbf{x}) = \sum_{\mathbf{R}\mathbf{R}'\mu\nu} \hat{c}_{\mathbf{R}\mu}^\dagger \hat{c}_{\mathbf{R}'\nu} \int d\mathbf{x} w_{\mathbf{R}\mu}^*(\mathbf{x}) \hat{h}(\mathbf{x}) w_{\mathbf{R}'\nu}(\mathbf{x}) \\ h_{\mu\nu}^{\mathbf{R}-\mathbf{R}'} &\equiv \int d\mathbf{x} w_{\mathbf{R}\mu}^*(\mathbf{x}) \hat{h}(\mathbf{x}) w_{\mathbf{R}'\nu}(\mathbf{x}) \end{aligned} \quad (72)$$

Dependence only on the difference  $\mathbf{R} - \mathbf{R}'$  follows from translational invariance. The Hamiltonian in eq. 72 is straightforward to diagonalize. In analogy with transforming the Bloch functions into Wannier states, we define the operator transformation

$$\begin{aligned} \hat{c}_{\mathbf{k}\mu}^\dagger &= N^{-1/2} \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot (\mathbf{R} + \boldsymbol{\tau}_\mu)) \hat{c}_{\mathbf{R}\mu}^\dagger \\ \hat{c}_{\mathbf{k}\mu} &= N^{-1/2} \sum_{\mathbf{R}} \exp(-i\mathbf{k} \cdot (\mathbf{R} + \boldsymbol{\tau}_\mu)) \hat{c}_{\mathbf{R}\mu} \end{aligned}$$

whereby eq. 72 becomes

$$\begin{aligned} \hat{H} &= \sum_{\mathbf{R}\mathbf{R}'\mu\nu} \hat{c}_{\mathbf{R}\mu}^\dagger \hat{c}_{\mathbf{R}'\nu} h_{\mu\nu}^{\mathbf{R}-\mathbf{R}'} = \\ &N^{-1} \sum_{\mathbf{k}\mathbf{k}'\mu\nu} \hat{c}_{\mathbf{k}\mu}^\dagger \hat{c}_{\mathbf{k}'\nu} \exp(i\mathbf{k} \cdot \boldsymbol{\tau}_\mu - i\mathbf{k}' \cdot \boldsymbol{\tau}_\nu) \sum_{\mathbf{R}\mathbf{R}'} h_{\mu\nu}^{\mathbf{R}-\mathbf{R}'} \exp(i\mathbf{k} \cdot \mathbf{R} - i\mathbf{k}' \cdot \mathbf{R}') \end{aligned}$$

Let  $\mathbf{R} \rightarrow \mathbf{R}'' + \mathbf{R}'$ . Then

$$\begin{aligned} &N^{-1} \sum_{\mathbf{R}\mathbf{R}'} h_{\mu\nu}^{\mathbf{R}-\mathbf{R}'} \exp(-i\mathbf{k}' \cdot \mathbf{R}' + i\mathbf{k} \cdot \mathbf{R}) = \\ &N^{-1} \sum_{\mathbf{R}''} h_{\mu\nu}^{\mathbf{R}''} \exp(i\mathbf{k} \cdot \mathbf{R}'') \sum_{\mathbf{R}'} \exp(-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}') = \\ &\delta_{\mathbf{k}\mathbf{k}'} \sum_{\mathbf{R}} h_{\mu\nu}^{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R}) \end{aligned}$$

It is very common to rewrite the symbol  $h_{\mu\nu}^{\mathbf{R}} = -t_{\mu\nu}(\mathbf{R})$ . It is called a “hopping parameter” because it corresponds to the amplitude for a particle on site  $\nu$  in the unitcell at the origin to tunnel, or “hop”, to site  $\mu$  in the unitcell at  $\mathbf{R}$ . Then

$$\begin{aligned}\hat{H} &= \sum_{\mathbf{k}} \sum_{\mu\nu} \hat{c}_{\mathbf{k}\mu}^\dagger \hat{c}_{\mathbf{k}\nu} \gamma_{\mu\nu}(\mathbf{k}) = \sum_{\mathbf{k}} \hat{H}_{\mathbf{k}} \\ \hat{H}_{\mathbf{k}} &= \sum_{\mu\nu} \hat{c}_{\mathbf{k}\mu}^\dagger \hat{c}_{\mathbf{k}\nu} \gamma_{\mu\nu}(\mathbf{k}) \\ \gamma_{\mu\nu}(\mathbf{k}) &= -\exp(i\mathbf{k} \cdot (\boldsymbol{\tau}_\mu - \boldsymbol{\tau}_\nu)) \sum_{\mathbf{R}} t_{\mu\nu}(\mathbf{R}) \exp(i\mathbf{k} \cdot \mathbf{R}) \\ t_{\mu\nu}(\mathbf{R}) &= \int d\mathbf{x} w_\mu^*(\mathbf{R}) \hat{h}(\mathbf{x}) w_\nu(0)\end{aligned}$$

The one-body Hamiltonian is decoupled into subspaces indexed by  $\mathbf{k}$ . This is convenient, but we still haven't quite solved the problem. Let us introduce the “vectors”

$$\begin{aligned}\hat{\Psi}_{\mathbf{k}}^\dagger &= (\hat{c}_{\mathbf{k}1}^\dagger, \hat{c}_{\mathbf{k}2}^\dagger, \dots, \hat{c}_{\mathbf{k}N}^\dagger) \\ \hat{\Psi}_{\mathbf{k}} &= (\hat{c}_{\mathbf{k}1}, \hat{c}_{\mathbf{k}2}, \dots, \hat{c}_{\mathbf{k}N})^T\end{aligned}$$

Then

$$\hat{H}_{\mathbf{k}} = \hat{\Psi}_{\mathbf{k}}^\dagger \hat{\mathcal{H}}_{\mathbf{k}} \hat{\Psi}_{\mathbf{k}} = \begin{pmatrix} \hat{c}_{\mathbf{k}1}^\dagger & \hat{c}_{\mathbf{k}2}^\dagger & \dots & \hat{c}_{\mathbf{k}N}^\dagger \end{pmatrix} \begin{pmatrix} \gamma_{11}(\mathbf{k}) & \gamma_{12}(\mathbf{k}) & \dots & \gamma_{1N}(\mathbf{k}) \\ \gamma_{21}(\mathbf{k}) & \gamma_{22}(\mathbf{k}) & \dots & \gamma_{2N}(\mathbf{k}) \\ \vdots & \vdots & \ddots & \vdots \\ \gamma_{N1}(\mathbf{k}) & \gamma_{N2}(\mathbf{k}) & \dots & \gamma_{NN}(\mathbf{k}) \end{pmatrix} \begin{pmatrix} \hat{c}_{\mathbf{k}1} \\ \hat{c}_{\mathbf{k}2} \\ \vdots \\ \hat{c}_{\mathbf{k}N} \end{pmatrix}$$

We proceed by diagonalizing  $\hat{\mathcal{H}}_{\mathbf{k}}$  by unitary transformation. Let  $\hat{U}_{\mathbf{k}}$  be the unitary matrix that diagonalizes  $\hat{\mathcal{H}}_{\mathbf{k}}$ . Call  $\hat{U}_{\mathbf{k}}^\dagger \hat{\mathcal{H}}_{\mathbf{k}} \hat{U}_{\mathbf{k}} \equiv \hat{\mathcal{K}}_{\mathbf{k}}$  the diagonal representation of  $\hat{\mathcal{H}}_{\mathbf{k}}$ . Then

$$\hat{H}_{\mathbf{k}} = \hat{\Psi}_{\mathbf{k}}^\dagger \hat{\mathcal{H}}_{\mathbf{k}} \hat{\Psi}_{\mathbf{k}} = \hat{\Psi}_{\mathbf{k}}^\dagger \hat{U}_{\mathbf{k}} \hat{U}_{\mathbf{k}}^\dagger \hat{\mathcal{H}}_{\mathbf{k}} \hat{U}_{\mathbf{k}} \hat{U}_{\mathbf{k}}^\dagger \hat{\Psi}_{\mathbf{k}} = \hat{\Phi}_{\mathbf{k}}^\dagger \hat{\mathcal{K}}_{\mathbf{k}} \hat{\Phi}_{\mathbf{k}}$$

The new vectors are

$$\begin{aligned}\hat{\Phi}_{\mathbf{k}}^\dagger &= \hat{\Psi}_{\mathbf{k}}^\dagger \hat{U}_{\mathbf{k}} = (\hat{d}_{\mathbf{k}1}^\dagger, \hat{d}_{\mathbf{k}2}^\dagger, \dots, \hat{d}_{\mathbf{k}Na}^\dagger) \\ \hat{d}_{\mathbf{k}\alpha}^\dagger &= \sum_{\beta} \hat{c}_{\mathbf{k}\beta}^\dagger U_{\mathbf{k}}^{\beta\alpha} \\ \hat{\Phi}_{\mathbf{k}} &= \hat{U}_{\mathbf{k}}^\dagger \hat{\Psi}_{\mathbf{k}} = (\hat{d}_{\mathbf{k}1}, \hat{d}_{\mathbf{k}2}, \dots, \hat{d}_{\mathbf{k}N})^T \\ \hat{d}_{\mathbf{k}\alpha} &= \sum_{\beta} \hat{c}_{\mathbf{k}\beta} [U_{\mathbf{k}}^\dagger]^{\alpha\beta}\end{aligned}$$

Let the diagonal elements of  $\hat{\mathcal{K}}_{\mathbf{k}}$  be called  $\epsilon_{\mathbf{k}n}$  with  $n$  a “band” index. Then

$$\hat{H}_{\mathbf{k}} = \hat{\Phi}_{\mathbf{k}}^\dagger \hat{\mathcal{K}}_{\mathbf{k}} \hat{\Phi}_{\mathbf{k}} = \sum_n \hat{d}_{\mathbf{k}n}^\dagger \hat{d}_{\mathbf{k}n} \epsilon_{\mathbf{k}n} = \sum_n \hat{n}_{\mathbf{k}n} \epsilon_{\mathbf{k}n}$$

We have solved the model! E.g. Taking the expectation value of this with respect to the groundstate determines the groundstate energy:

$$\mathcal{E} = \langle \Omega | \hat{H} | \Omega \rangle = \sum_{\mathbf{k}} \langle \Omega | \hat{H}_{\mathbf{k}} | \Omega \rangle = \sum_{\mathbf{k}n} \epsilon_{\mathbf{k}n} \langle \Omega | \hat{n}_{\mathbf{k}n} | \Omega \rangle = \sum_{\mathbf{k}n} n_{\mathbf{k}n} \epsilon_{\mathbf{k}n}$$

$n_{\mathbf{k}n}$  is the “occupation” of the state with quantum numbers  $\mathbf{k}, n$ . For Fermions, it is the Fermi-Dirac function; for Bosons, it is the Bose-Einstein distribution.

### 7.5.2 Interacting Hamiltonian

Let us now introduce a two-body interaction. From here on, we specialize to symmetric local interactions. The interaction Hamiltonian looks like<sup>20</sup>

$$\begin{aligned} \hat{H}_{int} &= \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}') \hat{\psi}(\mathbf{x}) U(|\mathbf{x} - \mathbf{x}'|) = \\ &\sum_{\mathbf{R}\mathbf{R}'\mathbf{T}\mathbf{T}'} \sum_{\mu\nu\lambda\gamma} \hat{c}_{\mathbf{R}\mu}^\dagger \hat{c}_{\mathbf{R}'\nu}^\dagger \hat{c}_{\mathbf{T}\lambda} \hat{c}_{\mathbf{T}'\gamma} \left( \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' w_{\mathbf{R}\mu}^*(\mathbf{x}) w_{\mathbf{R}'\nu}^*(\mathbf{x}') w_{\mathbf{T}\lambda}(\mathbf{x}') w_{\mathbf{T}'\gamma}(\mathbf{x}) U(|\mathbf{x} - \mathbf{x}'|) \right) \quad (73) \\ &\equiv \sum_{\mathbf{R}\mathbf{R}'\mathbf{T}\mathbf{T}'} \sum_{\mu\nu\lambda\gamma} \hat{c}_{\mathbf{R}\mu}^\dagger \hat{c}_{\mathbf{R}'\nu}^\dagger \hat{c}_{\mathbf{T}\lambda} \hat{c}_{\mathbf{T}'\gamma} U_{\mathbf{R}\mathbf{R}'\mathbf{T}\mathbf{T}'}^{\mu\nu\lambda\gamma} \end{aligned}$$

where the last line is the tight-binding representation. The factor of 1/2 in front is to compensate for double-counting the interaction. The interaction written in tight-binding affords a natural interpretation for localized electrons. Each term represents the energy “cost” for particles on two sites to interact, scattering onto two other sites. Moreover, it provides a natural path to an increasingly complex hierarchy of approximations.

Suppose we are studying electrons. Label their spins by  $\sigma$ . The tight-binding one-body Hamiltonian is

$$\hat{H}_0 = \sum_{\mathbf{R}\mathbf{R}'\mu\nu\sigma} \hat{c}_{\mathbf{R}\mu\sigma}^\dagger \hat{c}_{\mathbf{R}'\nu\sigma} t_{\mu\nu}(\mathbf{R} - \mathbf{R}')$$

The hopping is independent of spin, so we just sum over spin channels. The two body interaction is

$$\begin{aligned} \hat{H}_{int} &= \sum_{\mathbf{R}\mathbf{R}'\mathbf{T}\mathbf{T}'} \sum_{\mu\nu\lambda\gamma} \sum_{\sigma\sigma'} \hat{c}_{\mathbf{R}\mu\sigma}^\dagger \hat{c}_{\mathbf{R}'\nu\sigma'}^\dagger \hat{c}_{\mathbf{T}\lambda\sigma} \hat{c}_{\mathbf{T}'\gamma\sigma'} U_{\mathbf{R}\mathbf{R}'\mathbf{T}\mathbf{T}'}^{\mu\nu\lambda\gamma} \\ U_{\mathbf{R}\mathbf{R}'\mathbf{T}\mathbf{T}'}^{\mu\nu\lambda\gamma} &= \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' w_{\mathbf{R}\mu\sigma}^*(\mathbf{x}) w_{\mathbf{R}'\nu\sigma'}^*(\mathbf{x}') w_{\mathbf{T}\lambda\sigma}(\mathbf{x}') w_{\mathbf{T}'\gamma\sigma}(\mathbf{x}) U(|\mathbf{x} - \mathbf{x}'|) \end{aligned}$$

We won't need to keep track of the spin dependence of the interaction, so we drop the dependence in the symbol  $U_{\mathbf{R}\mathbf{R}'\mathbf{T}\mathbf{T}'}^{\mu\nu\lambda\gamma}$ . Let us flesh this interaction out and look at the important terms.

The so-called “direct” term

$$U_{\mathbf{R}\mathbf{R}'\mathbf{T}\mathbf{T}'}^{\mu\nu\lambda\gamma} \rightarrow U_{\mathbf{R}\mathbf{R}'}^{\mu\nu} = \frac{1}{2} \int d\mathbf{x} d\mathbf{x}' |w_{\mathbf{R}\mu\sigma}(\mathbf{x})|^2 |w_{\mathbf{R}'\nu\sigma'}(\mathbf{x}')|^2 U(|\mathbf{x} - \mathbf{x}'|)$$

<sup>20</sup> Need to check the order of operators wrt. position vs. eq. 69. The way this one is written is convenient below, but likely is off by a minus sign from the correct eq. written in 69...



is basically the classical Coulomb repulsion between electrons on different (neighboring) sites. The interaction is commonly labeled  $U_{\mathbf{R}\mathbf{R}'}^{\mu\nu} = V_{\mathbf{R}\mathbf{R}'}^{\mu\nu}$ .

$$\hat{H}_C = \sum_{\mathbf{R} \neq \mathbf{R}'} \sum_{\mu \neq \nu} \hat{n}_{\mathbf{R}\mu} \hat{n}_{\mathbf{R}'\nu} V_{\mathbf{R}\mathbf{R}'}^{\mu\nu}$$

where  $\hat{n}_{\mathbf{R}\mu} = \sum_{\sigma} \hat{c}_{\mathbf{R}\mu}^{\dagger} \hat{c}_{\mathbf{R}\mu}$  is the density. We dropped the dependence of the interaction on spin since it is irrelevant in the sums over spins.

Another important interaction is

$$\hat{H}_J = \sum_{\mathbf{R} \neq \mathbf{R}'} \sum_{\mu \neq \nu} \sum_{\sigma \sigma'} \hat{c}_{\mathbf{R}\mu\sigma}^{\dagger} \hat{c}_{\mathbf{R}'\nu\sigma'}^{\dagger} \hat{c}_{\mathbf{R}\mu\sigma'} \hat{c}_{\mathbf{R}'\nu\sigma} J_{\mathbf{R}\mathbf{R}'}^{\mu\nu}$$

which is, basically, swapping particles on *neighboring* sites. It is called an “exchange” interaction. Temporarily dropping unitcell dependence for convenience and replacing  $\sigma, \sigma'$  with  $\alpha, \beta, \gamma, \lambda$  as spin indices, we can write

$$\sum_{\alpha\beta} \hat{c}_{\mu\alpha}^{\dagger} \hat{c}_{\nu\beta}^{\dagger} \hat{c}_{\mu\beta} \hat{c}_{\nu\alpha} = - \sum_{\alpha\beta} \hat{c}_{\mu\alpha}^{\dagger} \hat{c}_{\mu\beta} \hat{c}_{\nu\beta}^{\dagger} \hat{c}_{\nu\alpha} = - \sum_{\alpha\beta\gamma\lambda} \hat{c}_{\mu\alpha}^{\dagger} \hat{c}_{\mu\beta} \hat{c}_{\nu\gamma}^{\dagger} \hat{c}_{\nu\lambda} \delta_{\alpha\lambda} \delta_{\beta\gamma}$$

We can use the Pauli matrix identity  $\boldsymbol{\sigma}_{\alpha\beta} \cdot \boldsymbol{\sigma}_{\gamma\lambda} = 2\delta_{\alpha\lambda}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\lambda}$ , where  $\boldsymbol{\sigma}_{\alpha\beta} = \hat{x}\sigma_{\alpha\beta}^x + \hat{y}\sigma_{\alpha\beta}^y + \hat{z}\sigma_{\alpha\beta}^z$  are (matrix elements of) the vectors of Pauli matrices, to simplify this. Rearranging, we have

$$\begin{aligned} - \sum_{\alpha\beta\gamma\lambda} \hat{c}_{\mu\alpha}^{\dagger} \hat{c}_{\mu\beta} \hat{c}_{\nu\gamma}^{\dagger} \hat{c}_{\nu\lambda} \delta_{\alpha\lambda} \delta_{\beta\gamma} &= -\frac{1}{2} \sum_{\alpha\beta\gamma\lambda} (\hat{c}_{\mu\alpha}^{\dagger} \boldsymbol{\sigma}_{\alpha\beta} \hat{c}_{\mu\beta}) \cdot (\hat{c}_{\nu\gamma}^{\dagger} \boldsymbol{\sigma}_{\gamma\lambda} \hat{c}_{\nu\lambda}) - \frac{1}{2} \sum_{\alpha\gamma} \hat{c}_{\mu\alpha}^{\dagger} \hat{c}_{\mu\alpha} \hat{c}_{\nu\gamma}^{\dagger} \hat{c}_{\nu\gamma} \\ &= -2 \left( \hat{\mathbf{S}}_{\mu} \cdot \hat{\mathbf{S}}_{\nu} + \frac{1}{4} \hat{n}_{\mu} \hat{n}_{\nu} \right) \end{aligned}$$

where  $\hat{\mathbf{S}}_{\mu} = \frac{1}{2} \sum_{\alpha\beta} \hat{c}_{\mu\alpha}^{\dagger} \boldsymbol{\sigma}_{\alpha\beta} \hat{c}_{\mu\beta}$  is the spin operator for site  $\mu$ . Putting this all back into  $\hat{H}_J$ , we have

$$\hat{H}_J = -2 \sum_{\mathbf{R} \neq \mathbf{R}'} \sum_{\mu \neq \nu} J_{\mathbf{R}\mathbf{R}'}^{\mu\nu} \left( \hat{\mathbf{S}}_{\mathbf{R}\mu} \cdot \hat{\mathbf{S}}_{\mathbf{R}'\nu} + \frac{1}{4} \hat{n}_{\mathbf{R}\mu} \hat{n}_{\mathbf{R}'\nu} \right) \quad (74)$$

We found that an effective magnetic coupling arose due to a purely electrostatic Coulomb interaction! This is a common property of magnetic ordering in solids and can be understood from the requirement of an antisymmetric wavefunction: the Coulomb repulsion between electrons on neighboring sites is smallest if the real-space wavefunction is antisymmetric (i.e. there is a node in the overlap region). Then the requirement that the total wavefunction (space+spin) be antisymmetric forces the spins to be parallel (i.e. symmetric). This heuristic rule is called “Hund’s rule” in atomic physics. In this case, the coupling leads to ferromagnetic ordering; regardless, all kinds of magnetic ordering in solids usually arise from an *exchange* interaction.

The last interaction we will consider (and one of the most famous ones!) is the *Hubbard interaction*. If we assume that the electrons are very localized, then we can ignore the

interactions between electrons on neighboring sites and consider only the on-site terms

$$U_{\mathbf{R}\mathbf{R}'\mathbf{T}\mathbf{T}'}^{\mu\nu\lambda\gamma} \rightarrow \frac{1}{2}U_{\mathbf{R}}^{\mu}$$

$$U_{\mathbf{R}}^{\mu} = \int d\mathbf{x}d\mathbf{x}' |w_{\mathbf{R}\mu\sigma}(\mathbf{x})|^2 |w_{\mathbf{R}\mu\sigma'}(\mathbf{x}')|^2 U(|\mathbf{x} - \mathbf{x}'|)$$

The factor of 1/2 was popped out for notational convenience below. Sometimes the potential  $U(|\mathbf{x} - \mathbf{x}'|)$  is replaced by a contact-interaction pseudopotential  $U(|\mathbf{x} - \mathbf{x}'|) \equiv \lambda\delta(\mathbf{x} - \mathbf{x}')$  where  $\lambda$  characterizes the strength of the interaction. Then

$$U_{\mathbf{R}}^{\mu} = \lambda \int d\mathbf{x}d\mathbf{x}' |w_{\mathbf{R}\mu\sigma}(\mathbf{x})|^2 |w_{\mathbf{R}\mu\sigma'}(\mathbf{x}')|^2 \delta(\mathbf{x} - \mathbf{x}') = \lambda \int d\mathbf{x} |w_{\mathbf{R}\mu\sigma}(\mathbf{x})|^2 |w_{\mathbf{R}\mu\sigma'}(\mathbf{x})|^2$$

$$\sim \lambda \int d\mathbf{x} |w_{\mathbf{R}\mu}(\mathbf{x})|^4$$

where the last line holds if the Wannier functions are independent of spin. Regardless, the Hubbard interaction Hamiltonian can be written

$$\hat{H}_U = \frac{1}{2} \sum_{\mathbf{R}\mu} \sum_{\sigma\sigma'} U_{\mathbf{R}}^{\mu} \hat{c}_{\mathbf{R}\mu\sigma}^{\dagger} \hat{c}_{\mathbf{R}\mu\sigma'}^{\dagger} \hat{c}_{\mathbf{R}\mu\sigma'} \hat{c}_{\mathbf{R}\mu\sigma}$$

For particles on the same site, we have (dropping site index for convenience)

$$\sum_{\sigma\sigma'} \hat{c}_{\sigma}^{\dagger} \hat{c}_{\sigma'}^{\dagger} \hat{c}_{\sigma'} \hat{c}_{\sigma} = - \sum_{\sigma\sigma'} \hat{c}_{\sigma}^{\dagger} \hat{c}_{\sigma'}^{\dagger} \hat{c}_{\sigma} \hat{c}_{\sigma'} = - \sum_{\sigma\sigma'} \hat{c}_{\sigma}^{\dagger} \left( \delta_{\sigma\sigma'} - \hat{c}_{\sigma} \hat{c}_{\sigma'}^{\dagger} \right) \hat{c}_{\sigma'} =$$

$$-\hat{n} + \sum_{\sigma\sigma'} \hat{n}_{\sigma} \hat{n}_{\sigma'} = -\hat{n} + \hat{n}_{\uparrow} \hat{n}_{\uparrow} + \hat{n}_{\downarrow} \hat{n}_{\downarrow} + \hat{n}_{\downarrow} \hat{n}_{\uparrow} + \hat{n}_{\uparrow} \hat{n}_{\downarrow}$$

Recalling that, for Fermions,  $\hat{n}^2 = \hat{n}$ , we have  $\hat{n}_{\uparrow} \hat{n}_{\uparrow} + \hat{n}_{\downarrow} \hat{n}_{\downarrow} = \hat{n}_{\uparrow} + \hat{n}_{\downarrow} = \hat{n}$ . Then

$$\sum_{\sigma\sigma'} \hat{c}_{\sigma}^{\dagger} \hat{c}_{\sigma'}^{\dagger} \hat{c}_{\sigma'} \hat{c}_{\sigma} = \hat{n}_{\downarrow} \hat{n}_{\uparrow} + \hat{n}_{\uparrow} \hat{n}_{\downarrow} = 2\hat{n}_{\downarrow} \hat{n}_{\uparrow}$$

and

$$\hat{H}_U = \sum_{\mathbf{R}\mu} U_{\mathbf{R}}^{\mu} \hat{n}_{\mathbf{R}\mu\downarrow} \hat{n}_{\mathbf{R}\mu\uparrow} \quad (75)$$

The fact that we only look at repulsion between opposite spins follows from the exclusion principle (see eq. 21 and the following paragraph). Electrons with same spin can't be at the same position, so have negligible Coulomb interaction. However, there is no such restriction on electrons with the same spin. With this in mind, we probably could have guessed eq. 75 from purely phenomenological grounds.

We have looked at the “direct” Coulomb interaction, the exchange interaction, and the Hubbard interaction. Of course, this list is not exhaustive. There are many other interactions of interest: the bond-charge interaction, the pair-hopping, etc. [23]. Moreover, if we have multiple orbitals on the same site, then we have to account for intra-orbital Hubbard interactions like in eq. 75 plus *inter*-orbital Hubbard interactions as well as on-site exchange (see eq. 19 in [17]) and the analogous generalization for the direct Coulomb interaction etc. Also see ref. [78] for spin-orbit coupling in tight-binding as well as an example of a multi-orbital calculation with pair-hopping.

### 7.5.3 Mean-Field-Theory for The Hubbard Model

Very often, we will want to know e.g. the density in the  $\mu^{th}$  “orbital,” i.e. the density on the  $\mu^{th}$  site. We can construct this by (inverse) Fourier transforming the density.

## 7.6 Many-Body Green Functions

The issue with many body quantum mechanics is that it is impossible to solve any problems ... instead, as we saw in eq. single particle quantum mechanics, we can study the Green function to learn about the excitations (eigenvalues of the Hamiltonian) in the system. So then let us now generalize the discussion of the GF in quantum mechanics to interacting systems.

I honestly don't know where these come from, but their physical interpretation is straightforward and it is easy to verify that they satisfy some nice properties. Let's do it now. First of all, the retarded many body Green function (i.e. RGF, we won't talk about the one particle version much more, so there shouldn't be confusion) is defined by

$$G^R(\mathbf{x}_f, \mathbf{x}_i; t_f - t_i) = -\frac{i}{\hbar} \langle \Omega | \hat{\psi}(\mathbf{x}_f, t_f) \hat{\psi}^\dagger(\mathbf{x}_i, t_i) - \hat{\psi}^\dagger(\mathbf{x}_i, t_i) \hat{\psi}(\mathbf{x}_f, t_f) | \Omega \rangle \theta(t_f - t_i)$$

$|\Omega\rangle$  is the ground-state of the system. The physical interpretation of this is straightforward: a particle is “created” at  $\mathbf{x}_i$  at  $t_i$  and is later removed from the position  $\mathbf{x}_f$  at  $t_f$ . The expectation value with the ground-state is the probability for this process to occur. It looks like nonsense that we would need to know the ground state to calculate this, but as we will see, this is an inessential problem. Anyway, let us check a few things. Obviously this is 0 for  $t_f < t_i$ . Now, recalling  $[\hat{\psi}(\mathbf{x}, t), \hat{\psi}^\dagger(\mathbf{x}', t)] = \delta(\mathbf{x} - \mathbf{x}')$  we can see that

$$\lim_{t_f \rightarrow t_i} G^R(\mathbf{x}_f, \mathbf{x}_i; t_f - t_i) = -\frac{i}{\hbar} \langle \Omega | [\hat{\psi}(\mathbf{x}_f, t), \hat{\psi}^\dagger(\mathbf{x}_i, t)] | \Omega \rangle = -\frac{i}{\hbar} \delta(\mathbf{x}_f - \mathbf{x}_i)$$

i.e. the many body generalization satisfies the correct boundary condition. Also note that, in the *non-interacting* case, the field operators satisfy the (Heisenberg) equation of motion

$$\partial_t \hat{\psi}(\mathbf{x}) = \frac{i}{\hbar} [\hat{H}, \hat{\psi}(\mathbf{x})] = -\frac{i\hbar}{2m_e} \frac{\partial^2 \hat{\psi}}{\partial \mathbf{x}^2}$$

Then we can calculate... **Not done...** The advanced GF is defined analogously.

The previous definitions are sensible, but a more convenient form to work with will usually be the *time-ordered* Green function (TOGF). It is defined as

$$G(\mathbf{x}_f, \mathbf{x}_i; t_f - t_i) = -\frac{i}{\hbar} \langle \Omega | \mathcal{T} \{ \hat{\psi}(\mathbf{x}_f, t_f) \hat{\psi}^\dagger(\mathbf{x}_i, t_i) \} | \Omega \rangle \quad (76)$$

with  $\mathcal{T}\{\dots\}$  the “Wick time-ordering operator”<sup>21</sup>. For Bosons fields, it is defined as

$$\mathcal{T} \{ \hat{\psi}(\mathbf{x}_f, t_f) \hat{\psi}^\dagger(\mathbf{x}_i, t_i) \} = \begin{cases} \hat{\psi}(\mathbf{x}_f, t_f) \hat{\psi}^\dagger(\mathbf{x}_i, t_i) & \text{if } t_f > t_i \\ \hat{\psi}^\dagger(\mathbf{x}_i, t_i) \hat{\psi}(\mathbf{x}_f, t_f) & \text{if } t_i > t_f \end{cases} \quad (77)$$

<sup>21</sup> It's not really an “operator” because it doesn't act on any Hilbert space; rather, it is a notational convenience that is introduced for reasons that will be apparent later.

For Fermion fields, we have to account for the anti-commutative nature of the fields; the time ordering operator is

$$\mathcal{T}\{\hat{\psi}(\mathbf{x}_f, t_f)\hat{\psi}^\dagger(\mathbf{x}_i, t_i)\} = \begin{cases} \hat{\psi}(\mathbf{x}_f, t_f)\hat{\psi}^\dagger(\mathbf{x}_i, t_i) & \text{if } t_f > t_i \\ -\hat{\psi}^\dagger(\mathbf{x}_i, t_i)\hat{\psi}(\mathbf{x}_f, t_f) & \text{if } t_i > t_f \end{cases} \quad (78)$$

The TOGF is a physically sensible thing to study. For the top-line in eq. 77 or eq. 78, we are investigating a particle that is injected into the system; it propagates through the system, interacting (and taking all paths...) along the way, then emerges *at a later time*. For the bottom line, we remove a particle and then study the dynamics of a *hole*. In either case, causality has to be respected. Note that we cannot know if it is the *same* particle/hole that emerges/re-enters at a later time.

## 7.7 The Many-Body Path Integral for Bosons

## 7.8 The Many-Body Path Integral (Redux)

Our goal is to now extend the concept of that path integral from quantum mechanics (eqs. 49 and 51) to quantum field theory; i.e. in particular, we want to formulate the path integral in terms of creation and annihilation operators (the field operators we met before!). There are many reasons for this, but the primary one is that the path integral formulation of quantum mechanics doesn't allow particle-number to fluctuate; in condensed matter settings, variable number of particles is a given. Considering that the Hamiltonian is expressed in terms of creation and annihilation operators, it should be apparent that we need to find the eigenstates of the creation and annihilation operators: the so called *coherent states*.

### 7.8.1 Coherent States

The formalism differs slightly depending on whether or not the particles are Bosons or Fermions. Let's do Bosons first. Since the number states  $|n_1, n_2, \dots\rangle$  form a complete set, we assume that we can write a coherent state as

$$|\phi\rangle \equiv \sum_{n_1, n_2, \dots} c_{n_1, n_2, \dots} |n_1, n_2, \dots\rangle$$

i.e. as a superposition of states with different particle numbers in them. Recall that

$$|n_1, n_2, \dots\rangle = \frac{(\hat{a}_1^\dagger)^{n_1}}{\sqrt{n_1!}} \frac{(\hat{a}_2^\dagger)^{n_2}}{\sqrt{n_2!}} \dots |0\rangle$$

We find that  $\hat{a}_i^\dagger$  adds a particle to every number state in the sum. Thus for e.g. a coherent state with a minimum of  $n_i$  particles in the  $i^{th}$  state,  $\hat{a}_i^\dagger |n_1, n_2, \dots\rangle$  has a minimum of  $n_i + 1$  particles in the  $i^{th}$  state. The  $\hat{a}^\dagger$  operators cannot have eigenstates! On the other hand, apparently the  $\hat{a}$  operators *do* have eigenstates and they are<sup>22</sup>

$$|\phi\rangle = \exp\left(\sum_i \phi_i \hat{a}_i^\dagger\right) |0\rangle \quad (79)$$

---

<sup>22</sup> I admittedly don't know how to derive these and I am too lazy to go figure it out right now. See footnote 1 in §4.1 in ref. [4].

The  $\phi_i$  are complex numbers; the eigenvalue of  $\hat{a}_i$  is  $\hat{a}_i|\phi\rangle = \phi_i|\phi\rangle$ . By taking the complex conjugate of eq. 79, we can also find that  $\langle\phi|\hat{a}_i^\dagger = \langle\phi|\phi_i^*$ . The “left eigenstate” is

$$\begin{aligned}\langle\phi| &= \langle 0| \exp\left(\sum_i \phi_i^* \hat{a}_i\right) \\ \exp\left(\sum_i \phi_i \hat{a}_i^\dagger\right) &= 1 + \sum_i \phi_i \hat{a}_i^\dagger + \frac{1}{2} \left(\sum_i \phi_i \hat{a}_i^\dagger\right)^2 + \cdots \\ \hat{a}_j \exp\left(\sum_i \phi_i \hat{a}_i^\dagger\right) &= \hat{a}_j + \hat{a}_j \sum_i \phi_i \hat{a}_i^\dagger + \hat{a}_j \frac{1}{2} \left(\sum_i \phi_i \hat{a}_i^\dagger\right)^2 + \cdots \\ &= \hat{a}_j|0\rangle + \hat{a}_j \sum_i \phi_i \hat{a}_i^\dagger|0\rangle =\end{aligned}$$

## 7.9 Generating Functional

Cardy’s notes, §3.2, Gurarie’s notes, and Burdman’s notes. Cardy describes adding a source as “tickling” the vacuum; we have to add a tiny perturbation to create excitations, then study the excitations. Correlation functions are calculated as functional derivatives with respect to the source: just like in usual calculus, in functional calculus we can study the (linear-)response of a functional by taking a derivative. At the end, the source is set to 0, i.e. the limit of an infinitesimal perturbation.

## 8 Examples

In this section, we study example problems related to the theory discussed throughout. It is logically cleaner to separate “examples” from “applications” with applications being actual research projects related to this document.

### 8.1 Electron-Phonon Coupling

In this subsection, we work through an example to highlight some common technical details of working with electron-phonon coupling models. The problem is a dumbed down version of ‘Electron-Phonon Coupling’ on pg. 187 in Altland and Simmons, ref. [4].

The phonon Hamiltonian is

$$\begin{aligned}\hat{H}_{ph} &= \sum_q \omega_q \hat{a}_q^\dagger \hat{a}_q + \frac{1}{2} \\ &\sim \sum_q \omega_q \hat{a}_q^\dagger \hat{a}_q\end{aligned}$$

and the electron Hamiltonian is

$$\hat{H}_e = \sum_k \epsilon_k \hat{c}_k^\dagger \hat{c}_k.$$

Both are one dimensional with only one mode (or “band”). We implicitly absorb the chemical potential  $\mu$  into  $\epsilon_k$ . The electron-phonon interaction is (skipping the derivation of the interaction)

$$\hat{H}_{eph} = g \sum_{kq} \hat{c}_{k+q}^\dagger \hat{c}_k \left( \hat{a}_q + \hat{a}_{-q}^\dagger \right) = g \sum_q \hat{n}_q \left( \hat{a}_q + \hat{a}_{-q}^\dagger \right).$$

The physical interpretation is that the electronic density,  $\hat{n}_q = \sum_k \hat{c}_{k+q}^\dagger \hat{c}_k$ , couples to a displacement of the “medium”,  $\hat{u}_q = \hat{a}_q + \hat{a}_{-q}^\dagger$ . The partition function is

$$Z(T) = \int \mathcal{D}[a^*, a] \mathcal{D}[c^*, c] \exp(-S[c^*, c, a^*, a])$$

with  $S[c^*, c, a^*, a]$  the “coherent state” action:

$$\begin{aligned}S[c^*, c, a^*, a] &= S_e[c^*, c] + S_{ph}[a^*, a] + S_{eph}[c^*, c, a^*, a] \\ S_e[c^*, c] &= \sum_k \int_0^\beta d\tau c_k^*(\tau) [\partial_\tau + \epsilon_k] c_k(\tau) \\ S_{ph}[a^*, a] &= \sum_q \int_0^\beta d\tau a_q^*(\tau) [\partial_\tau + \omega_q] a_q(\tau) \\ S_{eph}[a^*, a] &= g \sum_q \int_0^\beta d\tau n_q(\tau) [a_q(\tau) + a_{-q}^*(\tau)]\end{aligned}$$

We wish to “integrate out” the Bosons. To do so, we want to make use of the (Bosonic) Gaussian integral identity:

$$Z(\hat{K}, \mathbf{f}, \mathbf{j}) \equiv \int \mathcal{D}[z^*, z] \exp(-z^\dagger \hat{K} z + \mathbf{f}^\dagger \cdot \mathbf{z} + \mathbf{z}^\dagger \cdot \mathbf{j}) = Z_0(\hat{K}) \exp(\mathbf{f}^\dagger \hat{K}^{-1} \mathbf{j}) \quad (80)$$

$$Z_0(\hat{K}) = \frac{\pi^N}{\det[\hat{K}]}$$

$\mathbf{z}$  are complex Boson fields and  $\mathbf{f}$ ,  $\mathbf{j}$  are external “currents”. The matrix  $\hat{K}$  is Hermitian. The action isn’t in the correct form to apply the integral identity yet; we can get it there by Matsubara transforming the fields. The Matsubara transform is defined by

$$\psi(\tau) = \beta^{-1/2} \sum_n \psi(\omega_n) \exp(-i\omega_n \tau)$$

$$\psi(\omega_n) = \beta^{-1/2} \int_0^\beta d\tau \psi(\tau) \exp(i\omega_n \tau).$$

The “Matsubara frequencies” are different for Fermions and Bosons:

$$\omega_n = \begin{cases} (2n+1)\pi T & \text{Fermions} \\ 2n\pi T & \text{Bosons.} \end{cases}$$

To avoid confusion with the phonon energy  $\omega_q$ , we label the Bosonic Matsubara frequencies as  $\Omega_n$ . The (free) electron and (free) phonon actions become

$$S_e[c^*, c] = \sum_{nk} c_k^*(\omega_n) c_k(\omega_n) [-i\omega_n + \epsilon_k]$$

$$S_{ph}[a^*, a] = \sum_{mq} a_q^*(\Omega_m) a_q(\Omega_m) [-i\Omega_m + \omega_q].$$

The interaction term requires more care. First, rewrite it as

$$S_{eph}[c^*, c, a^*, a] = g \sum_q \int_0^\beta d\tau n_q(\tau) [a_q(\tau) + a_{-q}^*(\tau)] \equiv$$

$$g \sum_q \int_0^\beta d\tau f_q(\tau) a_q(\tau) + g \sum_q \int_0^\beta d\tau j_q(\tau) a_q^*(\tau)$$

with the “currents”  $f_q(\tau) \equiv \sum_k c_{k+q}^*(\tau) c_k(\tau)$  and  $j_q(\tau) \equiv \sum_k c_{k-q}^*(\tau) c_k(\tau)$ . The Matsubara transform of the current is

$$f_q(\tau) = \sum_k c_{k+q}^*(\tau) c_k(\tau) = \beta^{-1} \sum_{mnk} c_{k+q}^*(\omega_n) c_k(\omega_m) \exp(-i(\omega_m - \omega_n)\tau)$$

Sticking this into one of the part of the electron-phonon action, we find

$$\begin{aligned}
& \sum_q \int_0^\beta d\tau f_q(\tau) a_q(\tau) = \\
& \beta^{-1/2} \sum_{mnl} \sum_{kq} c_{k+q}^*(\omega_n) c_k(\omega_m) a_q(\Omega_l) \left( \beta^{-1} \int_0^\beta d\tau \exp(-i(\Omega_l - (\omega_n - \omega_m))\tau) \right) = \\
& \beta^{-1/2} \sum_{mnl} \sum_{kq} c_{k+q}^*(\omega_n) c_k(\omega_m) a_q(\Omega_l) \delta((\Omega_l + \omega_m) - \omega_n) = \\
& \beta^{-1/2} \sum_{mn} \sum_{kq} c_{k+q}^*(\omega_m + \Omega_n) c_k(\omega_m) a_q(\Omega_n).
\end{aligned}$$

Similarly,

$$\begin{aligned}
& \sum_q \int_0^\beta d\tau j_q(\tau) a_q^*(\tau) = \\
& \beta^{-1/2} \sum_{mn} \sum_{kq} c_{k-q}^*(\omega_m - \Omega_n) c_k(\omega_m) a_q^*(\Omega_n).
\end{aligned}$$

Then

$$S_{eph}[c^*, c, a^*, a] = \frac{g}{\beta^{1/2}} \left( \sum_{nq} f_q(\Omega_n) a_q(\Omega_n) + \sum_{nq} j_q(\Omega_n) a_q^*(\Omega_n) \right)$$

where  $f_q(\Omega_n) \equiv \sum_{mk} c_{k+q}^*(\omega_m + \Omega_n) c_k(\omega_m)$  and  $j_q(\Omega_n) \equiv \sum_{mk} c_{k-q}^*(\omega_m - \Omega_n) c_k(\omega_m)$ . Define the “four-vectors”  $\mathbb{k} \equiv (\omega_n, k)$  and  $\mathbb{q} \equiv (\Omega_n, q)$  (in this case, actually *two*-vectors since we are in  $1 + 1d$ ). The whole action becomes

$$\begin{aligned}
S_e[c^*, c] &= \sum_{\mathbb{k}} c^*(\mathbb{k}) c(\mathbb{k}) [-i\omega_n + \epsilon_k] \equiv \sum_{\mathbb{k}} c^*(\mathbb{k}) c(\mathbb{k}) H(\mathbb{k}) \\
S_{ph}[a^*, a] &= \sum_{\mathbb{q}} a^*(\mathbb{q}) a(\mathbb{q}) [-i\Omega_n + \omega_q] \equiv \sum_{\mathbb{q}} a^*(\mathbb{q}) a(\mathbb{q}) K(\mathbb{q}) \\
S_{eph}[c^*, c, a^*, a] &= \frac{g}{\beta^{1/2}} \left( \sum_{\mathbb{q}} f(\mathbb{q}) a(\mathbb{q}) + \sum_{\mathbb{q}} j(\mathbb{q}) a^*(\mathbb{q}) \right)
\end{aligned}$$

and the phonon coordinates can be integrated using eq. 80. Note that  $\hat{K} \rightarrow K(\mathbb{q}) \equiv -i\Omega_n + \omega_q$  is diagonal. Then

$$\begin{aligned}
Z(T) &= \int \mathcal{D}[c^*, c] \exp(-S_e[c^*, c]) \int \mathcal{D}[a^*, a] \exp(-S_{ph}[a^*, a] - S_{eph}[c^*, c, a^*, a]) = \\
& Z_0^{ph}(T) \int \mathcal{D}c \mathcal{D}c^* \exp(-S_e[c^*, c]) \exp \left( \frac{g^2}{\beta} \sum_{\mathbb{q}} \frac{f(\mathbb{q}) j(\mathbb{q})}{-i\Omega_n + \omega_q} \right)
\end{aligned}$$

the argument of the second exponential is the effective interaction:  $f(\mathbb{q})$  and  $j(\mathbb{q})$  are electronic density operators in the effective Hamiltonian. Fourier transforming the  $\omega$  dependence back to (imaginary) time, you get a non-local (in time) electron-electron interaction. This



works in real-time too by analytic continuation from imaginary to real time (or from imaginary to real frequencies.) In ref. [4],  $g = i\gamma q/(2m\omega_q)^{1/2}$ . Then

$$\frac{g^2}{\beta} \sum_{\mathbf{q}} \frac{f(\mathbf{q})j(\mathbf{q})}{-i\Omega_n + \omega_q} = -\frac{\gamma^2}{2m\beta} \sum_{nq} \frac{q^2 n_q(\Omega_n) n_{-q}(-\Omega_n)}{\omega_q (-i\Omega_n + \omega_q)} = \dots$$

allegedly this leads to the correct answer, but I don't see how yet. Anyway, I figured out what I needed to. Maybe I'll finish this later.

## 9 Additional Reading

- Tight-binding electron-phonon coupling: [7–9, 15, 76]
- Very good derivation of phonon-mediated electron-electron interaction by integrating out phonons [45]. I want to flip this and get an effective electron-electron interaction...

for discussion of how symmetry can be used to reduce k-point grid, see notes by Sigrist [68].

## 10 Electron-Phonon Coupling

In sec. 2.1.1, we saw that the electronic and nuclear sectors of the many-body Hamiltonian can be decoupled in the *adiabatic approximation*. This usually works well, but there are cases when we have to go beyond the adiabatic approximation. We study that here.

## A Matrix Multiplication

I frequently forget what indices go where in sums, so I am gonna write down matrix multiplication formulas here. Suppose we are working in  $2D$ ; the generalization to higher dimensions is obvious. Suppose we two a column vectors  $\mathbf{v} = (v_1, v_2)^T$  and  $\mathbf{x} = (x_1, x_2)^T$ . Also let  $\hat{A}$ ,  $\hat{B}$ , and  $\hat{C}$  be  $2 \times 2$  matrices:

$$\hat{A} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \quad \hat{B} = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} \quad \hat{C} = \begin{pmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{pmatrix}$$

Some formulas:

$$\mathbf{v} = \hat{A} \cdot \mathbf{x} = \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

$$v_i = \sum_j A_{ij} x_j$$

Similarly

$$\mathbf{v}^T = \mathbf{x}^T \cdot \hat{A} = (v_1 \ v_2) = (x_1 \ x_2) \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix}$$

$$v_i = \sum_j A_{ji} x_j$$

and

$$c = \mathbf{x}^T \cdot \hat{A} \cdot \mathbf{v} = (x_1 \ x_2) \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix}$$

$$\mathbf{w} = \hat{A} \cdot \mathbf{v}$$

$$c = \sum_i x_i w_i = \sum_{ij} x_i A_{ij} v_j$$

Lastly

$$\hat{C} = \hat{A} \hat{B} = \begin{pmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix}$$

$$C_{ij} = \sum_{kl} A_{ik} B_{kl}$$

## B Gaussian Integrals for Bosons

Some very common integrals we will encounter are “Gaussian integrals.” We work out the integral identities here. All of the integrals below are valid for *Bosonic fields*; this is because it is assumed throughout that the variables commute; this is not true for *Fermionic fields* which are Grassmann numbers. We will do the Fermionic Gaussian integrals in §C

In the following, an integral with no bounds explicitly written means to integrate from  $-\infty$  to  $\infty$ . Also pay particular attention to the argument of the symbol  $Z(*)$  where  $*$  denotes the argument; the particular integral being evaluated, and the nature of the coordinates, depend on the argument. Return to the definition at the beginning of each section if there is any confusion.

## B.1 Gaussian Integrals in 1-Dimension

As a warm up, and because the results later will depend on these, let us do the important 1-D Gaussian integrals first.

### B.1.1 Real Gaussian Integral

The first and simplest case is

$$Z_0(a) = \int dx \exp(-ax^2/2)$$

We can do this by noting that

$$Z_0^2(a) = \left( \int dx \exp(-ax^2/2) \right)^2 = \int dx dy \exp(-a(x^2 + y^2)/2)$$

We can integrate this by going to polar coordinates.

$$Z_0^2(a) = \int_0^{2\pi} d\phi \int_0^\infty dr r \exp(-ar^2/2) = 2\pi \int_0^\infty dr r \exp(-ar^2/2)$$

Letting  $r^2 \rightarrow u$ ,  $du = 2rdr$ , we have

$$Z_0^2(a) = \pi \int_0^\infty du \exp(-au/2) = -\frac{2\pi}{a} [\exp(-au/2)]_0^\infty$$

So finally,

$$\boxed{Z_0(a) = \sqrt{\frac{2\pi}{a}}} \quad (81)$$

### B.1.2 Gaussian With External Field

As a more complicated but still common case, let us add an “external field”.

$$Z_0(a, b) = \int dx \exp(-ax^2/2 + bx)$$

We can do this integral by “completing the square.”

$$-\frac{ax^2}{2} + bx = - \left[ \left( \sqrt{\frac{a}{2}}x - \sqrt{\frac{2}{a}}\frac{b}{2} \right)^2 - \frac{b^2}{2a} \right]$$

Then we have

$$Z_0(a, b) = \exp(b^2/2a) \int dx \exp(-(\sqrt{a/2}x - b/2\sqrt{a/2})^2)$$

This time, we let  $u = (\sqrt{a/2}x - b/2\sqrt{a/2})$ . Then  $du = \sqrt{a/2}dx$ . The remaining integral is just eq. 81 with  $a \rightarrow 2$ . Then

$$\boxed{Z_0(a, b) = \sqrt{\frac{2\pi}{a}} \exp\left(\frac{b^2}{2a}\right) = Z_0(a) \exp\left(\frac{b^2}{2a}\right)} \quad (82)$$

### B.1.3 “2-Point” Function

In higher dimensions, a very common integral involves products of integrals of the form

$$Z_1(a) = \int dx x^2 \exp(-ax^2/2)$$

Note that

$$Z_1(a) = -2 \frac{\partial}{\partial a} \int dx \exp(-ax^2/2) = -2 \frac{\partial}{\partial a} Z_0(a)$$

Taking the derivative, we find

$$Z_1(a) = \frac{1}{a} \sqrt{\frac{2\pi}{a}}$$

Then

$$\boxed{Z_1(a) = \frac{1}{a} Z_0(a)} \quad (83)$$

Note that there is an alternative and equally useful way to do this integral. We go back to the integral with external field

$$Z_0(a, b) = \int dx \exp(-ax^2/2 + bx)$$

and note that

$$\boxed{Z_1(a) = \left( \frac{\partial^2}{\partial b^2} Z_0(a, b) \right) \Big|_{b=0}} \quad (84)$$

### B.1.4 Complex Coordinates

Generalizing to  $a$  or  $b$  being complex poses no major challenge: e.g. with  $b \rightarrow ib$ , we obtain the Fourier transform of a Gaussian (a very useful quantity in LCAO calculations). More interesting is the generalization to complex coordinates,  $z$ . By virtue of  $z = x + iy$  having two degrees of freedom, the integration is actually over the whole of the complex plane. We will only consider integrals of the form

$$Z_0(h) \sim \int dx dy \exp(-h(x^2 + y^2))$$

where  $x^2 + y^2 = |z|^2 = z^* z$ . Note the missing factor of  $1/2$  in this definition; the reason for this definition will be clear when we introduce an external field. The primary reason to use this combination of coordinates in the exponential is physical; we demand the the action (see e.g. eq. 49) is real. Let us change coordinates to  $z$  and  $z^*$ . First of all, note that we can write

$$x = \frac{1}{2}(z + z^*) \quad y = -\frac{i}{2}(z - z^*)$$

The integration measure is

$$dx dy = \det \begin{pmatrix} \frac{\partial x}{\partial z} & \frac{\partial x}{\partial z^*} \\ \frac{\partial y}{\partial z} & \frac{\partial y}{\partial z^*} \end{pmatrix} dz^* dz = \frac{i}{2} dz^* dz$$

In what follows, we will neglect the *constant* factor  $i/2$  and simply consider integration over  $dz^*dz$  as independent coordinates. This is acceptable since physical quantities are always calculated as  $\langle O \rangle = Z_0^{-1} \int dz^*dz O(z, z^*) \exp(-h|z|^2)$  where the *constant* Jacobian drops out. The notation of integrating over  $dz^*dz$  is more for convenience; we actually do the integral over  $dxdy$  where we can immediately write down the answer:

$$\boxed{Z_0(h) = \int dz^*dz \exp(-h|z|^2) \sim \int dxdy \exp(-h(x^2 + y^2)) = \frac{\pi}{h}} \quad (85)$$

### B.1.5 Complex Coordinates With External Field

We now re-do the integral with external field. Let  $j \equiv j_1 + ij_2$  be complex. We need to integrate<sup>23</sup>

$$Z_0(h, j) = \int dz^*dz \exp(-h|z|^2 + jz^* + j^*z)$$

Go back to the  $x, y$  coordinates. Then

$$\begin{aligned} Z_0(h, j) &= \int dxdy \exp(-h(x^2 + y^2) + 2(j_1x + j_2y)) = \\ &= \int dx \exp(-hx^2 + 2j_1x) \int dy \exp(-hy^2 + 2j_2y) = \frac{\pi}{h} \exp\left(\frac{j_1^2 + j_2^2}{h}\right) \end{aligned}$$

So then finally

$$\boxed{Z_0(h, j) = Z_0(h) \exp\left(\frac{|j|^2}{h}\right)} \quad (86)$$

## B.2 Gaussian Integrals in N-Dimensions

In quantum field theory, we frequently encounter integrals that look like

$$\int \mathcal{D}\mathbf{x} \exp\left(-\frac{1}{2}\mathbf{x}^T \hat{A} \mathbf{x}\right)$$

where, in analogy to e.g. eq. 49, we define

$$\int \mathcal{D}\mathbf{x} \equiv \int dx_1 dx_2 \cdots dx_N$$

and

$$\mathbf{x}^T \hat{A} \mathbf{x} = \sum_{ij} A_{ij} x_i x_j$$

If the variables  $x_i$  are real, then  $\hat{A}$  is a real symmetric matrix. The elements of the matrix are  $[\hat{A}]_{ij} \equiv A_{ij}$ . If  $x_i \rightarrow z_i$  are complex,  $\hat{A} \rightarrow \hat{H}$  is a Hermitian matrix. We can generalize these to include external fields too. In that case, we will have an additional term

$$\mathbf{b}^T \cdot \mathbf{x} = \sum_i b_i x_i$$

---

<sup>23</sup> It is not required that we use the same external field in the different terms  $j^*z$  and  $z^*j$ . We could equally well use  $j^*z + z^*k$  with  $j$  and  $k$  different complex fields; we choose them to be the same for convenience.

in the exponential. Finally, we will do the integrals with factors  $\sim x^{2n}$  in the integrand. Let us work all these out in turn.

### B.2.1 Real Symmetric Matrix

As the first and simple case, we need to integrate

$$Z_0(\hat{A}) = \int \mathcal{D}\mathbf{x} \exp\left(-\frac{1}{2}\mathbf{x}^T \hat{A} \mathbf{x}\right)$$

with  $\mathbf{x}$  real and  $\hat{A}$  a real symmetric matrix. A physical example could be the partition function of a phonon-system: i.e.  $\mathbf{x}$  is atomic displacements and  $\hat{A}$  the force-constant matrix. Since  $\hat{A}$  is a real symmetric matrix, it can be diagonalized by an orthogonal transformation. Let  $\hat{D}$  be the diagonal matrix and  $\hat{O}$  be the orthogonal transformation matrix:  $\hat{O}^T \hat{O} \equiv 1$ . Then

$$\begin{aligned}\hat{D} &= \hat{O}^T \hat{A} \hat{O} \\ \hat{A} &= \hat{O} \hat{D} \hat{O}^T\end{aligned}$$

and

$$\begin{aligned}\mathbf{x}^T \hat{A} \mathbf{x} &= \mathbf{x}^T (\hat{O} \hat{D} \hat{O}^T) \mathbf{x} = (\mathbf{x}^T \hat{O}) \hat{D} (\hat{O}^T \mathbf{x}) \\ &\equiv \mathbf{y}^T \hat{D} \mathbf{y} = \sum_i D_{ii} y_i^2\end{aligned}$$

The diagonal elements of  $\hat{D} = D_{ii} \equiv \lambda_i$  are the “eigenvalues” of  $\hat{A}$ . We defined the new vectors  $\mathbf{y} = \hat{O}^T \mathbf{x}$ . Note that  $\mathbf{x} = \hat{O} \mathbf{y}$  with  $x_i = \sum_j O_{ij} y_j$ . The elements of  $\hat{O}$  are constants that depend only on  $\hat{A}$ . An arbitrary element of the Jacobian,  $\hat{J}$ , is then

$$J_{ij} = \frac{\partial x_i}{\partial y_j} = O_{ij}$$

The determinant of the Jacobian is  $\det[\hat{J}] = \det[\hat{O}] = 1$  which follows from the fact that  $\hat{O}$  is an orthogonal matrix. Then

$$\begin{aligned}Z_0(\hat{A}) &= \int \mathcal{D}\mathbf{x} \exp\left(-\frac{1}{2}\mathbf{x}^T \hat{A} \mathbf{x}\right) = \int \mathcal{D}\mathbf{y} \exp\left(-\frac{1}{2}\mathbf{y}^T \hat{D} \mathbf{y}\right) = \\ &\int dy_1 \exp\left(-\frac{1}{2}\lambda_1 y_1^2\right) \int dy_2 \exp\left(-\frac{1}{2}\lambda_2 y_2^2\right) \cdots \int dy_N \exp\left(-\frac{1}{2}\lambda_N y_N^2\right)\end{aligned}$$

So then we have decoupled the  $N$ -dimensional Gaussian integral into  $N$  1-dimensional Gaussian integrals that we already know how to do. The result is

$$Z_0(\hat{A}) = \sqrt{\frac{(2\pi)^N}{\prod_i \lambda_i}}$$

Now recalling the identity  $\det[\hat{A}] = \prod_i \lambda_i$ , we can rewrite this as

$$\boxed{Z_0(\hat{A}) = \sqrt{\frac{(2\pi)^N}{\prod_i \lambda_i}} = \sqrt{\frac{(2\pi)^N}{\det[\hat{A}]}}} \quad (87)$$



The second equality is the most general form, but the first is worth memorizing too since it is how the integral is calculated in practice; we diagonalize  $\hat{A}$  and can then evaluate the integral immediately.

### B.2.2 Real Symmetric Matrix With External Field

As a slightly more complicated case, consider

$$Z_0(\hat{A}, \mathbf{b}) = \int \mathcal{D}\mathbf{x} \exp \left( -\frac{1}{2} \mathbf{x}^T \hat{A} \mathbf{x} + \mathbf{b}^T \cdot \mathbf{x} \right)$$

We proceed as before. Let  $\mathbf{b}^T \cdot (\hat{O} \hat{O}^T) \cdot \mathbf{x} = (\mathbf{b}^T \hat{O}) \cdot (\hat{O}^T \mathbf{x})$ . We call  $\mathbf{b}^T \hat{O} \equiv \mathbf{v}^T$  and, as before,  $\hat{O}^T \mathbf{x} = \mathbf{y}$ . Then we have

$$\mathbf{b}^T \cdot \mathbf{x} = \sum_i b_i x_i = \mathbf{v}^T \cdot \mathbf{y} = \sum_i v_i y_i$$

The  $N$ -dimensional integral above becomes

$$\begin{aligned} Z_0(\hat{A}, \mathbf{b}) &= \int \mathcal{D}\mathbf{x} \exp \left( -\frac{1}{2} \mathbf{x}^T \hat{A} \mathbf{x} + \mathbf{b}^T \cdot \mathbf{x} \right) = \\ &= \int dy_1 \exp \left( -\frac{1}{2} \lambda_1 y_1^2 + v_1 y_1 \right) \cdots \int dy_N \exp \left( -\frac{1}{2} \lambda_N y_N^2 + v_N y_N \right) \end{aligned}$$

i.e. a product of  $N$  integrals, each identical to the 1-dimensional Gaussian integral with external field we did earlier: see eq. 82. Then

$$Z_0(\hat{A}, \mathbf{b}) = Z_0(\hat{A}) \exp \left( \frac{1}{2} \sum_i \frac{v_i^2}{\lambda_i} \right) = Z_0(\hat{A}) \exp \left( \frac{1}{2} \mathbf{v}^T \hat{D}^{-1} \mathbf{v} \right)$$

Where  $\hat{D}$  is the diagonal representation of  $\hat{A}$  from before. The inverse of a diagonal matrix is just a diagonal matrix with the elements  $1/\lambda_i$  along its diagonal. Note that  $\mathbf{v} = \hat{O}^T \mathbf{b}$ . Then

$$\begin{aligned} \mathbf{v}^T \hat{D}^{-1} \mathbf{v} &= \mathbf{b}^T (\hat{O} \hat{D}^{-1} \hat{O}^T) \mathbf{b} \\ \hat{O} \hat{D}^{-1} \hat{O}^T &= \hat{O} \hat{D}^{-1} \hat{O}^{-1} = [\hat{O} \hat{D} \hat{O}^T]^{-1} = \hat{A}^{-1} \end{aligned}$$

So then finally

$$\boxed{Z_0(\hat{A}, \mathbf{b}) = Z_0(\hat{A}) \exp \left( \frac{1}{2} \mathbf{b}^T \hat{A}^{-1} \mathbf{b} \right)} \quad (88)$$

Again, this is a very useful identity... but in practice, it is more practical to diagonalize  $\hat{A}$  and evaluate using the diagonal matrix.

### B.2.3 “2-Point” Function With Real Symmetric Matrix

Now consider

$$Z_{ij}(\hat{A}) = \int \mathcal{D}\mathbf{x} x_i x_j \exp \left( -\frac{1}{2} \mathbf{x}^T \hat{A} \mathbf{x} \right)$$

We can evaluate this by introducing the external field  $\mathbf{b}$ . We notice that

$$Z_{ij}(\hat{A}) = \frac{\partial^2}{\partial b_i \partial b_j} \left[ \int \mathcal{D}\mathbf{x} \exp \left( -\frac{1}{2} \mathbf{x}^T \hat{A} \mathbf{x} + \mathbf{b}^T \cdot \mathbf{x} \right) \right] \Big|_{\mathbf{b}=0} = \\ Z_0(\hat{A}) \frac{\partial^2}{\partial b_i \partial b_j} \left[ \exp \left( \frac{1}{2} \mathbf{b}^T \hat{A}^{-1} \mathbf{b} \right) \right] \Big|_{\mathbf{b}=0}$$

So then let us do the derivatives.

$$\frac{\partial^2}{\partial b_i \partial b_j} \exp \left( \frac{1}{2} \mathbf{b}^T \hat{A}^{-1} \mathbf{b} \right) = \frac{\partial^2}{\partial b_i \partial b_j} \exp \left( \frac{1}{2} \sum_{kl} b_k [\hat{A}^{-1}]_{kl} b_l \right) = \\ \frac{\partial}{\partial b_j} \left[ \exp \left( \frac{1}{2} \sum_{kl} b_k [\hat{A}^{-1}]_{kl} b_l \right) \sum_m [\hat{A}^{-1}]_{im} b_m \right]$$

where we used the fact that the inverse of a symmetric matrix is symmetric; i.e.  $[\hat{A}^{-1}]_{kl} = [\hat{A}^{-1}]_{lk}$ . Now do the next derivative

$$\frac{\partial}{\partial b_j} \left[ \exp \left( \frac{1}{2} \sum_{kl} b_k [\hat{A}^{-1}]_{kl} b_l \right) \sum_m [\hat{A}^{-1}]_{im} b_m \right] = \\ [\hat{A}^{-1}]_{ij} \exp \left( \frac{1}{2} \sum_{kl} b_k [\hat{A}^{-1}]_{kl} b_l \right) + \exp \left( \frac{1}{2} \sum_{kl} b_k [\hat{A}^{-1}]_{kl} b_l \right) \sum_{mn} [\hat{A}^{-1}]_{im} [\hat{A}^{-1}]_{jn} b_m b_n$$

Finally, setting  $\mathbf{b} = 0$ , we find

$$\boxed{Z_{ij}(\hat{A}) = \frac{\partial^2 Z_0(\hat{A}, \mathbf{b})}{\partial b_i \partial b_j} \Big|_{\mathbf{b}=0} = Z_0(\hat{A}) [\hat{A}^{-1}]_{ij}} \quad (89)$$

Note that, if we hadn't integrated over an even number of  $x$ 's, all terms occurring after taking the derivative above would vanish when setting  $\mathbf{b} = 0$ . What is (almost ubiquitously) encountered in practice is actually

$$\langle x_i x_j \rangle = \frac{Z_{ij}(\hat{A})}{Z_0(\hat{A})} = [\hat{A}^{-1}]_{ij}$$

i.e. we don't have to usually have to calculate the determinant in  $Z_0(\hat{A})$ . We hold off calculating higher order "correlation functions" until discussing Wick's theorem later.

#### B.2.4 Hermitian Matrix

We now generalize to let  $x \rightarrow z$  be complex variables. Then the matrix  $\hat{A} \rightarrow \hat{H}$  is Hermitian. The integral we need to do is

$$Z_0(\hat{H}) = \int \mathcal{D}\mathbf{z}^\dagger \mathcal{D}\mathbf{z} \exp \left( -\mathbf{z}^\dagger \hat{H} \mathbf{z} \right)$$

Here, the notation is

$$\int \mathcal{D}\mathbf{z}^\dagger \mathcal{D}\mathbf{z} = \int dz_1^* dz_1 dz_2^* dz_2 \cdots dz_N^* dz_N$$

A physical example of one of these integrals could be the partition function of an electronic system; we would have  $\mathbf{z}$  an electronic state vector and  $\hat{H}$  the Hamiltonian. Since  $\hat{H}$  is Hermitian, it can be diagonalized by a unitary transformation. Let  $\hat{K}$  be the diagonal matrix and  $\hat{U}$  be the unitary transformation matrix:  $\hat{U}^\dagger \hat{U} \equiv 1$ . The eigenvalues of  $\lambda_i$  are the real.

We define new vectors  $\mathbf{w} = \hat{U}^\dagger \mathbf{z}$  with  $\mathbf{z} = \hat{U} \mathbf{w}$  and  $\mathbf{w}^\dagger = \mathbf{z}^\dagger \hat{U}$  with  $\mathbf{z}^\dagger = \mathbf{w}^\dagger \hat{U}^\dagger$ . Then  $z_i = \sum_j U_{ij} w_j$  and  $z_k^* = \sum_l U_{lk}^* w_l^*$ . What is the Jacobian? Well, note that

$$\begin{aligned} \frac{\partial z_i^*}{\partial w_j^*} &= U_{ji}^* & \frac{\partial z_i^*}{\partial w_j} &= 0 \\ \frac{\partial z_i}{\partial w_j} &= U_{ij} & \frac{\partial z_i}{\partial w_j^*} &= 0 \end{aligned}$$

Then the Jacobian

$$\begin{pmatrix} U_{11}^* & \cdots & U_{N1}^* & 0 & \cdots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ U_{1N}^* & \cdots & U_{NN}^* & 0 & \cdots & 0 \\ 0 & \cdots & 0 & U_{11} & \cdots & U_{1N} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ 0 & \cdots & 0 & U_{N1} & \cdots & U_{NN} \end{pmatrix} \equiv \begin{pmatrix} \hat{U}^\dagger & 0 \\ 0 & \hat{U} \end{pmatrix}$$

is block-diagonal. The determinant of a block-diagonal matrix can be shown to be  $\det[\hat{A} \oplus \hat{B}] = \det[\hat{A}] \det[\hat{B}] = \det[\hat{A}\hat{B}]$ . For the Jacobian, then,  $\det[\hat{J}] = \det[\hat{U}^\dagger \hat{U}] = 1$ . Nice!<sup>24</sup>.

So finally, we can rewrite

$$\begin{aligned} Z_0(\hat{H}) &= \int \mathcal{D}\mathbf{z}^\dagger \mathcal{D}\mathbf{z} \exp(-\mathbf{z}^\dagger \hat{H} \mathbf{z}) = \int \mathcal{D}\mathbf{w}^\dagger \mathcal{D}\mathbf{w} \exp(-\mathbf{w}^\dagger \hat{K} \mathbf{w}) = \\ &= \int dw_1^* dw_1 \exp(-\lambda_1 |w_1|^2) \cdots \int dw_N^* dw_N \exp(-\lambda_N |w_N|^2) \end{aligned}$$

Each of these is a 1-dimensional Gaussian integrals over complex variables; we already learned how to do these. The result is

$$Z_0(\hat{H}) = \frac{\pi^N}{\prod_i \lambda_i} = \frac{\pi^N}{\det[\hat{H}]} \quad (90)$$

The second equality is the most general form, but the first is worth memorizing too since it is how the integral is calculated in practice; we diagonalize  $\hat{H}$  and can then evaluate the integral immediately.

<sup>24</sup> In principle, we could have just ignored the *constant* Jacobian since it would disappear in physical observables. This is what we did above for the  $-i/2$  in the 1-D Gaussian integral over complex variables.

### B.2.5 Hermitian Matrix With External Field

We now generalize the Hermitian Gaussian integral to include an external field. We let  $\mathbf{j}$  be a complex vector. The integral we need to do is<sup>25</sup>

$$Z_0(\hat{H}, \mathbf{j}) = \int \mathcal{D}\mathbf{z}^\dagger \mathcal{D}\mathbf{z} \exp \left( -\mathbf{z}^\dagger \hat{H} \mathbf{z} + \mathbf{j}^\dagger \cdot \mathbf{z} + \mathbf{z}^\dagger \cdot \mathbf{j} \right)$$

We proceed just like in the real symmetric case. Let  $\mathbf{t} = \hat{U}^\dagger \mathbf{j}$  and  $\mathbf{t}^\dagger = \mathbf{j}^\dagger \hat{U}$ . Also recall  $\mathbf{w} = \hat{U}^\dagger \mathbf{z}$  with  $\mathbf{z} = \hat{U} \mathbf{w}$  and  $\mathbf{w}^\dagger = \mathbf{z}^\dagger \hat{U}$  with  $\mathbf{z}^\dagger = \mathbf{w}^\dagger \hat{U}^\dagger$ . Then

$$\begin{aligned} Z_0(\hat{H}, \mathbf{j}) &= \int \mathcal{D}\mathbf{w}^\dagger \mathcal{D}\mathbf{w} \exp \left( -\mathbf{w}^\dagger \hat{K} \mathbf{w} + \mathbf{t}^\dagger \cdot \mathbf{w} + \mathbf{w}^\dagger \cdot \mathbf{t} \right) = \\ &= \int dw_1^* dw_1 \exp \left( -\lambda_1 |w_1|^2 + t_1^* w_1 + w_1^* t_1 \right) \cdots \int dw_N^* dw_N \exp \left( -\lambda_N |w_N|^2 + t_N^* w_N + w_N^* t_N \right) \end{aligned}$$

We can use eq. 86 to do all the 1-dimensional integrals.

$$Z_0(\hat{H}, \mathbf{j}) = Z_0(\hat{H}) \exp \left( \mathbf{t}^\dagger \hat{K}^{-1} \mathbf{t} \right)$$

We can now transform coordinates back and find

$$\boxed{Z_0(\hat{H}, \mathbf{j}) = Z_0(\hat{H}) \exp \left( \mathbf{j}^\dagger \hat{H}^{-1} \mathbf{j} \right)} \quad (91)$$

### B.2.6 “2-Point” Function With Hermitian Matrix

To complete this section, let us do

$$Z_{ij}(\hat{H}) = \int \mathcal{D}\mathbf{z}^\dagger \mathcal{D}\mathbf{z} z_i z_j^* \exp \left( -\mathbf{z}^\dagger \hat{H} \mathbf{z} \right)$$

In analogy with the real symmetric matrix, we can introduce a (complex) external field,  $\mathbf{j}$ , and take the derivative of  $Z_0(\hat{H}, \mathbf{j})$ , setting  $\mathbf{j} = 0$  at the end. Specifically

$$\begin{aligned} Z_{ij}(\hat{H}) &= \frac{\partial^2}{\partial j_i^* \partial j_j} \left[ \int \mathcal{D}\mathbf{z}^\dagger \mathcal{D}\mathbf{z} \exp \left( -\mathbf{z}^\dagger \hat{H} \mathbf{z} + \mathbf{j}^\dagger \cdot \mathbf{z} + \mathbf{z}^\dagger \cdot \mathbf{j} \right) \right] \Big|_{\mathbf{j}=0} = \\ &= Z_0(\hat{H}) \frac{\partial^2}{\partial j_i^* \partial j_j} \left[ \exp \left( \mathbf{j}^\dagger \hat{H}^{-1} \mathbf{j} \right) \right] \Big|_{\mathbf{j}=0} \end{aligned}$$

Let us work out the derivative.

$$\begin{aligned} \frac{\partial^2}{\partial j_i^* \partial j_j} \left[ \exp \left( \mathbf{j}^\dagger \hat{H}^{-1} \mathbf{j} \right) \right] &= \frac{\partial^2}{\partial j_i^* \partial j_j} \left[ \exp \left( \sum_{kl} [\hat{H}^{-1}]_{kl} j_k^* j_l \right) \right] = \\ &= \frac{\partial}{\partial j_j} \left[ \exp \left( \sum_{kl} [\hat{H}^{-1}]_{kl} j_k^* j_l \right) \sum_m [\hat{H}^{-1}]_{im} j_m \right] = \\ &= [\hat{H}^{-1}]_{ij} \exp \left( \sum_{kl} [\hat{H}^{-1}]_{kl} j_k^* j_l \right) + \exp \left( \sum_{kl} [\hat{H}^{-1}]_{kl} j_k^* j_l \right) \sum_{mn} [\hat{H}^{-1}]_{nj} [\hat{H}^{-1}]_{im} j_n^* j_m \end{aligned}$$

<sup>25</sup> We could instead use external fields terms like  $\mathbf{j}^\dagger \cdot \mathbf{z} + \mathbf{z}^\dagger \cdot \mathbf{k}$  with  $\mathbf{j}$  and  $\mathbf{k}$  different complex fields; they do *not* have to be the same field. We just make this choice for convenience.

Now, setting  $\mathbf{j} = 0$ , the second term vanishes. Note that if the integral is over (i) a different number of  $z$  than  $z^*$  or (ii) an odd number of both, the whole thing vanishes when setting  $\mathbf{j} = 0$ . So then we find that

$$\boxed{Z_{ij}(\hat{H}) = \left. \frac{\partial^2 Z_0(\hat{H}, \mathbf{j})}{\partial j_i^* \partial j_j} \right|_{\mathbf{j}=0} = Z_0(\hat{H})[\hat{H}^{-1}]_{ij}} \quad (92)$$

Just like discussed before, we will usually be more interested in

$$\langle z_i z_j^* \rangle = \frac{Z_{ij}(\hat{H})}{Z_0(\hat{H})} = [\hat{H}^{-1}]_{ij}$$

### B.3 Wick's Theorem

Follows lec. 13 in Romatschke's QFT notes. Wick's theorem provides a very important formula for doing Gaussian integrals in many-body perturbation theory. It tells how to calculate integrals of the form

$$\langle x_i x_j \cdots x_k \rangle = Z_0^{-1}(\hat{A}) \int \mathcal{D}\mathbf{x} x_i x_j \cdots x_k \exp\left(-\frac{1}{2} \mathbf{x}^T \hat{A} \mathbf{x} + \mathbf{b}^T \cdot \mathbf{x}\right)$$

Earlier, we learned how to do this with only two variables  $x$  under the integral; in this expression, we allow for an arbitrary but even number,  $n$ , of  $x$ 's. We want to evaluate this for both real symmetric  $\hat{A}$  and Hermitian  $\hat{A} \rightarrow \hat{H}$  (and we drop the  $1/2$ ). In the Hermitian case, we require an even number,  $n$ , of  $x \rightarrow z$ 's as well as requiring that there are an equal number of  $z$ 's as there are  $z^*$ 's.

How we will do these integrals is just like how we calculated 2-point functions above. We take derivatives of  $Z_0(\hat{A}, \mathbf{b})$ . Specifically, in analogy to eqs. 89 and 92, we recognize

$$\langle x_i x_j \cdots x_k \rangle = Z_0^{-1}(\hat{A}) \left. \frac{\partial^n Z_0(\hat{A}, \mathbf{b})}{\partial b_i \partial b_j \cdots \partial b_k} \right|_{\mathbf{b}=0} = \left[ \frac{\partial^n}{\partial b_i \partial b_j \cdots \partial b_k} \exp\left(\frac{1}{2} \mathbf{b}^T \hat{A}^{-1} \mathbf{b}\right) \right] \Big|_{\mathbf{b}=0}$$

We defined the “generating function”  $W(\hat{A}, \mathbf{b}) = \exp\left(\frac{1}{2} \mathbf{b}^T \hat{A}^{-1} \mathbf{b}\right)$  for notational convenience. Let us learn how to do these integrals now.

#### B.3.1 Real Symmetric Matrix

For the real symmetric case, we need to calculate

$$\langle x_i x_j \cdots x_k \rangle = \left. \frac{\partial^n W(\hat{A}, \mathbf{b})}{\partial b_i \partial b_j \cdots \partial b_k} \right|_{\mathbf{b}=0}$$

with the generating function

$$W(\hat{A}, \mathbf{b}) = \exp\left(\frac{1}{2} \mathbf{b}^T \hat{A}^{-1} \mathbf{b}\right)$$

$n$  is an even integer but is otherwise arbitrary. We proceed by Taylor expanding the generating function

$$W(\hat{A}, \mathbf{b}) = \exp\left(\frac{1}{2}\mathbf{b}^T \hat{A}^{-1} \mathbf{b}\right) = 1 + \frac{1}{2} \sum_{ij} [\hat{A}^{-1}]_{ij} b_i b_j + \frac{1}{8} \sum_{ijkl} [\hat{A}^{-1}]_{ij} [\hat{A}^{-1}]_{kl} b_i b_j b_k b_l + \dots$$

To get the  $0^{th}$  order term  $\langle 1 \rangle = 1$  we, trivially set  $\mathbf{b} = 0$ . Obviously if we take only one (or any odd order) derivative, the whole series vanishes when setting  $\mathbf{b} = 0$ . Then let us do  $2^{nd}$  order term: the so-called propagator, correlation function, 2-point function, Green function, etc. It is easy to see that all terms of higher order than the  $2^{nd}$  one will have  $b$ 's in them and thus vanish when setting  $\mathbf{b} = 0$ . So we can ignore those and only focus on the first two terms. It is easy to see that

$$\langle x_i x_j \rangle = [\hat{A}^{-1}]_{ij}$$

This is perfectly consistent with eq. 92. For the 4-point function  $\langle x_i x_j x_k x_l \rangle$ , we can use similar arguments as above to ignore higher order terms than the  $3^{rd}$  in the series. In fact, we can ignore the lower ones too. Then let us study only the relevant term. Specifically, we want to calculate

$$\frac{\partial^4}{\partial b_i \partial b_j \partial b_k \partial b_l} \sum_{mnpq} [\hat{A}^{-1}]_{mn} [\hat{A}^{-1}]_{pq} b_m b_n b_p b_q$$

As an intermediate step, let's first calculate

$$\begin{aligned} \frac{\partial}{\partial b_i} \sum_{mnpq} [\hat{A}^{-1}]_{mn} [\hat{A}^{-1}]_{pq} b_m b_n b_p b_q &= \sum_{npq} [\hat{A}^{-1}]_{in} [\hat{A}^{-1}]_{pq} b_n b_p b_q + \\ &\sum_{mpq} [\hat{A}^{-1}]_{mi} [\hat{A}^{-1}]_{pq} b_m b_p b_q + \sum_{mnq} [\hat{A}^{-1}]_{mn} [\hat{A}^{-1}]_{ip} b_m b_n b_q + \sum_{mnp} [\hat{A}^{-1}]_{mn} [\hat{A}^{-1}]_{qi} b_m b_n b_p \end{aligned}$$

Since  $\hat{A}^{-1}$  is symmetric, all of these terms are equivalent. Then we have

$$\frac{\partial}{\partial b_i} \sum_{mnpq} [\hat{A}^{-1}]_{mn} [\hat{A}^{-1}]_{qp} b_m b_n b_p b_q = 4 \sum_{mnp} [\hat{A}^{-1}]_{im} [\hat{A}^{-1}]_{np} b_m b_n b_p$$

Next, we need

$$\frac{\partial}{\partial x_j} \sum_{mnp} [\hat{A}^{-1}]_{im} [\hat{A}^{-1}]_{np} b_m b_n b_p = [\hat{A}^{-1}]_{ij} \sum_{np} [\hat{A}^{-1}]_{np} b_n b_p + 2 \sum_{mn} [\hat{A}^{-1}]_{im} [\hat{A}^{-1}]_{jn} b_m b_n$$

Obviously

$$\frac{\partial^2}{\partial x_k \partial x_l} \sum_{np} [\hat{A}^{-1}]_{np} b_n b_p = 2 [\hat{A}^{-1}]_{kl}$$

Next, let's do

$$\frac{\partial}{\partial b_k} \sum_{mn} [\hat{A}^{-1}]_{im} [\hat{A}^{-1}]_{jn} b_m b_n = \sum_n [\hat{A}^{-1}]_{ik} [\hat{A}^{-1}]_{jn} b_n + \sum_m [\hat{A}^{-1}]_{im} [\hat{A}^{-1}]_{jk} b_m$$

Then clearly

$$\frac{\partial^2}{\partial b_k \partial b_l} \sum_{mn} [\hat{A}^{-1}]_{im} [\hat{A}^{-1}]_{jn} b_m b_n = [\hat{A}^{-1}]_{ik} [\hat{A}^{-1}]_{jl} + [\hat{A}^{-1}]_{il} [\hat{A}^{-1}]_{jk}$$

Putting all of these back together, we have

$$\boxed{\langle x_i x_j x_k x_l \rangle = [\hat{A}^{-1}]_{ij} [\hat{A}^{-1}]_{kl} + [\hat{A}^{-1}]_{ik} [\hat{A}^{-1}]_{jl} + [\hat{A}^{-1}]_{il} [\hat{A}^{-1}]_{jk} = \langle x_i x_j \rangle \langle x_k x_l \rangle + \langle x_i x_k \rangle \langle x_j x_l \rangle + \langle x_i x_l \rangle \langle x_j x_k \rangle} \quad (93)$$

Note that the factor  $1/8$  canceled with the combinatorial factors in the derivatives of the sums. What we have found is that the 4-point function factors in a sum of products of 2-point functions with their indices permuted. One can show that a similar formula holds to arbitrary order<sup>26</sup>. Specifically, that an  $n$ -point function factors into a sum of all possible products of 2-point functions with permuted indices. i.e.

$$\boxed{\langle x_i x_j \cdots x_k x_l \rangle = \sum_{\mathcal{P}\{ij \cdots kl\}} [\hat{A}^{-1}]_{\sigma(i)\sigma(j)} \cdots [\hat{A}^{-1}]_{\sigma(k)\sigma(l)}} \quad (94)$$

The symbol  $\mathcal{P}\{ij \cdots kl\}$  means “all possible permutations of pairings of the indices”; the symbols  $\sigma(i)$  stand for “indices to be permuted.” If the meaning is unclear, return to eq. 93 above where the pairings are written explicitly for the case of 4 indices.

### B.3.2 Hermitian Matrix

For the Hermitian case, we need to calculate

$$\langle z_i z_j \cdots z_k z_l^* z_m^* \cdots z_n^* \rangle = \left. \frac{\partial^{2n} W(\hat{H}, \mathbf{j})}{\partial j_i^* \partial j_j^* \cdots \partial j_k^* \partial j_l \partial j_m \cdots \partial j_n} \right|_{\mathbf{b}=0}$$

with the generating function

$$W(\hat{H}, \mathbf{j}) = \exp \left( \mathbf{j}^\dagger \hat{H}^{-1} \mathbf{j} \right)$$

$n$  is an even integer and there are an equal number of  $z$  and  $z^*$ . Use

$$W(\hat{H}, \mathbf{j}) = 1 + \sum_{mn} [\hat{H}^{-1}]_{mn} j_m^* j_n + \frac{1}{2} \sum_{mnpq} [\hat{H}^{-1}]_{mn} [\hat{H}^{-1}]_{pq} j_m^* j_n j_p^* j_q + \cdots$$

Clearly  $\langle 1 \rangle = 1$  and  $\langle z_i z_j^* \rangle = [\hat{H}^{-1}]_{ij}$ , consistent with before. The 4-point function,  $\langle z_i z_j z_k^* z_l^* \rangle$ , is the lowest order non-trivial term; we need to calculate

$$\frac{\partial^4}{\partial j_i^* \partial j_j^* \partial j_k \partial j_l} \sum_{mnpq} [\hat{H}^{-1}]_{mn} [\hat{H}^{-1}]_{pq} j_m^* j_n j_p^* j_q$$

<sup>26</sup> A more general proof would probably use the multinomial theorem to write the expansion at arbitrary order; taking the derivatives of that will still be a mess, but doing it explicitly like for the 4-point function seems out of the question!

First, calculate

$$\frac{\partial}{\partial j_i^*} \sum_{mnpq} [\hat{H}^{-1}]_{mn} [\hat{H}^{-1}]_{pq} j_m^* j_n j_p^* j_q = 2 \sum_{mnp} [\hat{H}^{-1}]_{im} [\hat{H}^{-1}]_{np} j_m j_n^* j_p$$

Next, we need

$$\frac{\partial}{\partial j_j^*} \sum_{mnp} [\hat{H}^{-1}]_{im} [\hat{H}^{-1}]_{np} j_m j_n^* j_p = \sum_{mn} [\hat{H}^{-1}]_{im} [\hat{H}^{-1}]_{jn} j_m j_n$$

The final non-trivial step is

$$\frac{\partial}{\partial j_k} \sum_{mn} [\hat{H}^{-1}]_{im} [\hat{H}^{-1}]_{jn} j_m j_n = \sum_m \left( [\hat{H}^{-1}]_{ik} [\hat{H}^{-1}]_{jm} j_m + [\hat{H}^{-1}]_{im} [\hat{H}^{-1}]_{jk} j_m \right)$$

Here, the two different terms are not equivalent since we have already fixed the other indices. So finally, we have

$$\frac{\partial^4}{\partial j_i^* \partial j_j^* \partial j_k \partial j_l} \sum_{mnpq} [\hat{H}^{-1}]_{mn} [\hat{H}^{-1}]_{pq} j_m^* j_n j_p^* j_q = 2 \left( [\hat{H}^{-1}]_{ik} [\hat{H}^{-1}]_{jl} + [\hat{H}^{-1}]_{il} [\hat{H}^{-1}]_{jk} \right)$$

Putting all of these back together, we have

$$\boxed{\langle z_i z_j z_k^* z_l^* \rangle = [\hat{H}^{-1}]_{ik} [\hat{H}^{-1}]_{jl} + [\hat{H}^{-1}]_{il} [\hat{H}^{-1}]_{jk} = \langle z_i z_k^* \rangle \langle z_j z_l^* \rangle + \langle z_i z_l^* \rangle \langle z_j z_k^* \rangle} \quad (95)$$

For the arbitrary order  $n$ -point function, we have

$$\boxed{\langle z_a z_b \cdots z_c z_\alpha^* z_\beta^* \cdots z_\gamma^* \rangle = \sum_{\substack{\mathcal{P}\{ab\cdots c\} \\ \mathcal{P}\{\alpha\beta\cdots\gamma\}}} [\hat{A}^{-1}]_{\sigma(a)\sigma(\alpha)} [\hat{A}^{-1}]_{\sigma(b)\sigma(\beta)} \cdots [\hat{A}^{-1}]_{\sigma(c)\sigma(\gamma)}} \quad (96)$$

The symbol  $\mathcal{P}\{ab\cdots c\}$  means “all possible permutations of pairings of the Latin alphabet indices” and likewise for the Greek indices. Since the matrix  $\hat{H}^{-1}$  is Hermitian (as opposed to symmetric), we have to keep the Latin indices on the left and Greek ones on the right in the 2-point functions. The symbols  $\sigma(i)$  stand for “indices to be permuted.” If the meaning is unclear, return to eq. 95 above where the pairings are written explicitly for the case of 4 indices.



## C Gaussian Integrals for Fermions

## D Some Notes on Angular Momentum

In this section, we derive (or just write down) some stuff about angular momentum that is used above. The exposition is clear but with no particular goal.

### D.1 Addition of Angular Momentum

We suppose we have a system with total angular momentum  $\hat{\mathbf{L}}_T = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2$ , where  $\hat{\mathbf{L}}$  are vector angular momentum operators. If  $\hat{\mathbf{L}}$  measures *orbital* angular momentum, eigenstates of  $\hat{L}^2$  are the spherical harmonics  $\langle \mathbf{\Omega} | lm \rangle = Y_l^m(\mathbf{\Omega})$  with  $\mathbf{\Omega}$  a unit vector. The eigenvalue of  $\hat{L}^2$  is  $\hat{L}^2 | lm \rangle = l(l+1)\hbar^2 | lm \rangle$ . The commutators of the components are  $[\hat{L}_i, \hat{L}_j] = i\hbar \epsilon_{ijk} \hat{L}_k$  and of the components with  $\hat{L}^2$  are  $[\hat{L}^2, \hat{L}_i] = 0$ . Eigenstates of  $\hat{L}_z$  are also eigenstates of  $\hat{L}^2$ . The eigenvalues are  $\hat{L}_z | lm \rangle = m\hbar | lm \rangle$ .

For total angular momentum,  $\hat{L}_T^2 = \hat{L}_1^2 + \hat{L}_2^2 + 2\hat{\mathbf{L}}_1 \cdot \hat{\mathbf{L}}_2$ . The operators  $\hat{\mathbf{L}}_1$  and  $\hat{\mathbf{L}}_2$  clearly commute with  $\hat{\mathbf{L}}_T$  but  $\hat{L}_{1z}$  and  $\hat{L}_{2z}$  don't. So it turns out that only  $l_T, m_T$ , and  $l_1, l_2$  are still good quantum numbers (actually the set  $\{l_1, m_1; l_2, m_2\}$  are still good quantum numbers too, but we have to pick *one* of these sets. We wish to express eigenstates in the total angular momentum basis here). The eigenstates of total angular momentum can be written in the basis of product states  $|l_1 m_1\rangle \otimes |l_2 m_2\rangle \equiv |l_1 m_1; l_2 m_2\rangle$

$$|l_T m_T\rangle = \sum_{m_1, m_2} \langle l_1 m_1; l_2 m_2 | l_T m_T \rangle |l_1 m_1; l_2 m_2\rangle$$

The symbols  $\langle l_T m_T | l_1 m_1; l_2 m_2 \rangle$  are ‘‘Clebsch-Gordan’’ coefficients. They are the matrix elements of the transformation between the  $|l_T m_T\rangle$  and  $|l_1 m_1; l_2 m_2\rangle$  bases. Note that  $\hat{L}_{Tz} = \hat{L}_{1z} + \hat{L}_{2z}$ . Then obviously the following operator is zero:  $(\hat{L}_{Tz} - \hat{L}_{1z} - \hat{L}_{2z}) = 0$ . Then

$$\begin{aligned} \langle l_1 m_1; l_2 m_2 | (\hat{L}_{Tz} - \hat{L}_{1z} - \hat{L}_{2z}) | l_T m_T \rangle &= 0 \\ &= (m_T - m_1 - m_2) \langle l_1 m_1; l_2 m_2 | l_T m_T \rangle \end{aligned}$$

If  $m_T \neq m_1 + m_2$ , then the Clebsch-Gordan coefficient vanishes. The other requirement is that  $|l_1 - l_2| \leq l_T \leq l_1 + l_2$  which is practically obvious from the interpretation of  $l$  as a vector-magnitude.

### D.2 Rotations

Rotation matrices have a convenient representation in terms of spherical harmonics. Suppose we have a state-vector pointing along the positive  $z$ -axis,  $|\mathbf{z}\rangle$  that we wish to rotate to point along an arbitrary direction,  $\mathbf{\Omega}$ , with ket  $|\mathbf{\Omega}\rangle$ . These vectors are unit-normalized ‘‘direction eigenkets’’. We leave the ‘‘hat’’ off the unit-vectors to avoid confusion with operators. Denote the set of Euler angles for the rotation by  $\{\alpha, \beta, \gamma\} \equiv R$ . The rotation can be accomplished by (unitary) matrix multiplication. Call the rotation matrix  $\hat{D}(R)$ . Then  $|\mathbf{\Omega}\rangle = \hat{D}(R)|\mathbf{z}\rangle$ . Let us insert a complete set of states. Since angular momentum states,  $|lm\rangle$ , are eigenstates of a Hermetian operator, they form a complete basis. Then  $\hat{1} \equiv \sum_{lm} |lm\rangle \langle lm|$ .

$$|\mathbf{\Omega}\rangle = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} \hat{D}(R) |lm\rangle \langle lm | \mathbf{z} \rangle$$

Note that  $\hat{D}(R) \equiv \exp(-i\hat{\mathbf{L}} \cdot \mathbf{n}\phi/\hbar)$  is a function of  $\hat{\mathbf{L}}$  so that  $\hat{L}^2$  commutes with  $\hat{D}(R)$ . i.e. rotations do *not* mix  $l$  eigenstates. We can drop the sum over  $l$ . Hit the above equation on the left by  $\langle lm' |$ .

$$\langle lm' | \Omega \rangle = \sum_{m=-l}^{m=l} D_{m'm}^{(l)}(R) \langle lm | z \rangle$$

where  $D_{m'm}^{(l)} \equiv \langle lm' | \hat{D}(R) | lm \rangle$ . The superscript  $(l)$  indicates this acts on states with definite angular momentum  $l$  and does not mix them with other  $l'$ . Note that this is equivalent to

$$Y_l^{*m'}(\Omega) = \sum_{m=-l}^{m=l} D_{m'm}^{(l)}(R) Y_l^m(\theta=0, \phi)$$

But for  $\theta=0$ ,  $Y_l^m(\theta=0, \phi) = \sqrt{(2l+1)/(4\pi)} \delta_{m0}$ . Then we find that  $D_{m'0}^{(l)}(R) = \sqrt{4\pi/(2l+1)} Y_l^{*m'}(\Omega)$ .

Now let's look at something else. Consider the following object:

$$D_{m_1 m'_1}^{(l_1)}(R) D_{m_2 m'_2}^{(l_2)}(R) = \langle l_1 m_1; l_2 m_2 | \hat{D}(R) | l_1 m'_1; l_2 m'_2 \rangle$$

Let  $|l_T m_T\rangle$  be the total angular momentum basis.  $\sum_{lm} |l_T m_T\rangle \langle l_T m_T| = \hat{1}$  by completeness of angular momentum eigenfunctions. Then

$$\begin{aligned} D_{m_1 m'_1}^{(l_1)}(R) D_{m_2 m'_2}^{(l_2)}(R) &= \\ \sum_{l_T m_T} \sum_{l'_T m'_T} \langle l_1 m_1; l_2 m_2 | l_T m_T \rangle \langle l_T m_T | \hat{D}(R) | l'_T m'_T \rangle \langle l'_T m'_T | l_1 m'_1; l_2 m'_2 \rangle \\ &= \sum_{l_T} \sum_{m_T m'_T} D_{m_T m'_T}^{(l_T)}(R) \langle l_1 m_1; l_2 m_2 | l_T m_T \rangle \langle l_T m'_T | l_1 m'_1; l_2 m'_2 \rangle \end{aligned}$$

We can use this to prove some neat things about spherical harmonics. Recall that  $D_{m0}^{(l)}(R) = \sqrt{4\pi/(2l+1)} Y_l^{*m}(\Omega)$ . Also recall the selection rules for Clebsch-Gordan coefficients:  $\langle l_1 m_1; l_2 m_2 | LM \rangle$  is non-zero only if  $m_1 + m_2 = M$  and  $|l_1 - l_2| \leq L \leq l_1 + l_2$ . Then (after complex conjugating and noting that the Clebsch-Gordan coefficients are real)

$$\begin{aligned} Y_{l_1}^{m_1}(\Omega) Y_{l_2}^{m_2}(\Omega) &= \\ \sum_L' \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}} Y_L^M(\Omega) \langle l_1 0; l_2 0 | L 0 \rangle \langle l_1 m_1; l_2 m_2 | LM \rangle \end{aligned} \quad (97)$$

The prime symbol on the sum means only to sum over allowed values of  $L$ . This is already a very useful identity. We can use it to find even more stuff.

$$\begin{aligned} \int d\Omega Y_L^{*M}(\Omega) Y_{l_1}^{m_1}(\Omega) Y_{l_2}^{m_2}(\Omega) &\equiv \langle LM | l_1 m_1 | l_2 m_2 \rangle \\ &= \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}} \langle l_1 0; l_2 0 | L 0 \rangle \langle l_1 m_1; l_2 m_2 | LM \rangle \end{aligned} \quad (98)$$

This last equation, eq. 98, is called a “Gaunt coefficient.” Inserting eq. 98 into 97 simplifies the notation slightly:

$$Y_{l_1}^{m_1}(\boldsymbol{\Omega})Y_{l_2}^{m_2}(\boldsymbol{\Omega}) = \sum_L \langle LM|l_1m_1|l_2m_2\rangle Y_L^M(\boldsymbol{\Omega})$$

## E PhD Goals

Many-body perturbation theory of phonons. Phonon-phonon, electron-phonon, etc. [13, 29, 69] and look for changes in neutron experiments. Figure out how to calculate phonon spectral function. See e.g. these papers [33, 34, 39, 55, 88] and how changes to the spectral function will show up in a neutron experiment. Basically calculate the many-body  $S(\mathbf{Q}, \omega)$ . Look at Gurarie's HW 4, this is evaluated for a gas of bosons. It's probably pretty similar.

### E.1 Downfolding

See [11, 60, 65]. Also see [12] which gives a cool, simple 1d eph model.

### E.2 Electron-Phonon Coupling

See [3] for electron-phonon matrix element interpolation using atomic orbitals: this is analogous to the Wannier interpolation method used by EPW [29, 30]. Note also that QUANTUM ESPRESSO has started writing out the phonon-induced scattering potential that ABINIT uses to interpolate electron phonon coupling. In principle, I can use whatever basis functions I want and calculate electron-phonon matrix elements from the scattering potential.

#### E.2.1 Electron-Phonon Coupling in “Simple” Models

The following papers calculate the phonon spectral function to study renormalization under various circumstances (CDW, nesting, phonon-phonon anharmonicity...) [16, 20, 31, 49, 53, 77, 79]

### E.3 Current Projects

Project that Dmitry wants me to work on:

- Flash sintered  $\text{TiO}_2$ . They have diffuse scattering data from CORELLI and no one to work on it. I could model  $\text{TiO}_2$  under finite electric field and look at structural changes. Could do from DFT and try to do from MD. Basically need Born effective charges to study coupling of phonons to electric field. Here is a ref. for  $\text{TiO}_2$ : [26] and a general ref for MD with external E field: [25]

Projects we already have data for:

- $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ : We already have high quality INS data for  $x = 0.25$  and we still have Adrian's  $x = 0.33$  data. I have seen some recent papers on LSNO, so it's still of interest broadly. No one knows what's going on, same issue as in LSCO. In principle, I can just quickly go through the INS data and publish this without any modelling, but I prefer to at least try to include some calculations. *Discussion of the calculations, if applicable, can be done separately.*

The difference between LSNO and LSCO is that LSCO *does* have a Fermi surface, so it is possible to try to study phonon renormalization due to nesting. Giustino's

Nature paper tried it in the metallic GGA ground state which is not the same as e.g. GGA+U with doping. Maybe there is nesting in the GGA+U groundstate leading to the 'dip' observed by INS in the half-breathing branch. A possible path is to look for "momentum dependent electron-phonon coupling" instead of nesting [43]. An alternative exotic concept is spinon-phonon coupling: spinons are Fermions and could exhibit nesting. I found a little literature on spinon-phonon coupling [38, 56, 66, 83, 85]. In particular, ref. [83] derives the spinon-phonon coupling in tight-binding and calculates the "effective" phonon action integrated over spinon variables. Good starting point if we can justify assuming there are spinons in LSNO. That being said, I can't find compelling evidence for spinons in LSNO or even in planar cuprates... maybe if we can rigorously show that spinons lead to the phonon anomalies we observe, we can argue for there being spinons? Addendum: there is evidence for spin-excitation with a Fermi surface in the "resonating valence bond state" (RVB) [5, 56, 74]! Could even argue that very strong electron-phonon coupling in nickelates destroys the quasiparticles that are superconducting in the cuprates? More refs. for spinons in RVB state [10, 41, 82]. Possibly relevant: [46]. These folks observed an optical phonon damped into a broad continuum in the presence of CDW ordering in a Kagome metal. Not a similar material, but similar phonon anomaly.

- LaMnO<sub>3</sub>: Have INS data and needs support by modelling.
- Halide Perovskites: Have INS and MD data on MAPI, I did a bunch of DFT on CsPbBr<sub>3</sub> already. We know there is novel structural ordering and there is LOTS of interest in science community to study these materials. Many recent papers on polarons and electron-phonon interactions.

More on halide perovskites: see §2.2 in Zamaklar's notes. Vortices spontaneously appear over a certain temperature in the Kosterlitz-Thouless model. They lower the *free-energy* by increasing the entropy. It would be very instructive to work out the details of this applied to e.g. MAPI.

## E.4 Prospective projects

- Kagome metals: Compounds with stoichiometry  $AV_3Sb_5$  ( $A \in \{K, Rb, Cs\}$ ). Very new compounds (by Eric Toberer of all people...) [57]. They possess CDW/SDW ordering, magnetic frustration etc. People have observed electronic gaps induced by band-folding due to CDW ordering [48] but have notably not found Kohn-anomalies. Some groups have found an optical mode that is damped into a broad continuum [46]. See also [53].
- Kondo Insulators:  $f$  electrons with large  $U$  hybridize with (nominal) conduction bands, opening a small  $\sim 0.5eV$  gap. There should be phonon anomalies associated with the gap and they should respond strongly to doping. Haven't read too much into these yet, but have seen recent papers.
- Hot-phonon Physics: e.g. MgB<sub>2</sub>, Nick and Susmita's work on YBCO, boron doped diamond...

- Study phonon tunnelling in hybrid halide perovskites. They have soft modes at 0 energy transfer all over the Brillouin zone. Maybe this intensity is damped there by phonon tunneling. Could study electron-assisted phonon tunneling: affects mobilities. Use the TB electron phonon coupling idea as in here: [11, 15]
- anharmonically renormalized force constants: [36, 58, 70, 81, 84]

It seems that I ultimately keep circling back to the same stuff: phonons coupling to CDW. This is a very popular topic.

Finally there are a few other “miscellaneous” topics that I know I’ve been asked to work on. They are

- Local Temperature Probe: Devise a method to “measure” the local temperature e.g. in a solid-state circuit operating in steady state. The method would use diffuse scattering and “fit” e.g. thermal displacements to the diffuse background and measure the temperature.
- Teach you guys computational methods: I was asked to teach my lab mates about DFT and lattice dynamical calculations at least a year ago. This document (plus my mixed-basis notes) are the current status of that.
- Phonon Lifetimes from  $S(\mathbf{Q}, \omega)$ : Can use my MD code to extract lifetimes from gnarly superstructures. People often use “spectral-energy-density” (SED) method, but that folds all bands into the 1BZ. To resolve modes, they use lattice dynamics calculations and project the atomic velocities in SED onto the eigenvectors. It works, but the validity of using harmonic eigenvectors is questionable. Calculating  $S(\mathbf{Q}, \omega)$  is a very good alternative as it requires only minimal input from the user (but requires more knowledge about phonon physics and, in particular, neutron scattering). A relevant paper validating ab-initio anharmonic lifetime calculations is [79].

## F Neutron Scattering

moved this to different docs

## G Miscellaneous Notes

The action of the position operator,  $\hat{x}$ , on the wave-function is to multiply it by the position  $x$ .

$$\hat{x}\psi(x) = x\psi(x)$$

Refs for band unfolding: [18, 59]

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