Condensed Matter Physics
from the context of the courses
PHY 491: Solid State Physics

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October 12, 2022

Contents

0.1 The SI System

In physics it's often important to have precisely defined units for the purposes of making very accurate measurements or simply having a coherent unit system. It's possible to derive all necessary units from five measurements of **length, mass, time, current, and temperature**. The standard SI units for these properties are listed bellow:

Type	Unit	Definition
Length	Meter(m)	Length of distance light in a vacuum travels in $\frac{1}{299792458}$ seconds
Mass	Kilogram(kg)	Defined by fixing the Planck's constant $h = 6.62607015 \times 10^{-34} kg\ m^2 s^{-1}$
Time	Second(s)	Defined by fixing the ground-state hyperfine transition frequency of the caesium-133 atom, to be $9192631770 s^{-1}$
Current	Ampere(A)	Defined by fixing the charge of an electron as $1.602176634 \times 10^{-19} A \cdot s$
Temperature	Kelvin(K)	Defined by fixing the value of the Boltzmann constant k to $1.380649 \times 10^{-23} kg \cdot m^2 s^{-2} K^{-1}$

Common prefixes are listed bellow:

Prefix	Symbol	Definition
mega	M	10^6
kilo	k	10^3
milli	m	10^{-3}
micro	μ	10^{-6}
nano	n	10^{-9}
pico	p	10^{-12}
femto	f	10^{-15}

Additionally, the following are defined constants:

Symbol	Definition
$\hbar$	$\hbar = \frac{h}{2\pi} \approx 1.0546 \times 10^{-34} kg\ m^2 s^{-1}$

0.2 Why Study Condensed Matter

Condensed matter physics is the most broad field of physics that has a large overlap with other fields such as atomic physics, quantum physics, chemistry, and biology. Condensed matter physics describes anything that is "condensed" this includes any solid material, such as metals, glass, wood and electronics. As such it is very important in our world. Condensed

matter is simultaneously very fundamental describing microscopic sources for material properties such as superconductivity, charge density waves, topological insulators. These phenomenon can't be described by reductionism and many properties only emerge when you consider larger systems that cannot be solved using fundamental laws alone.

Chapter 1

Atoms and Molecules

1.1 Hydrogen Like Systems

Many systems in condensed matter are similar to the hydrogen atom system and so it is often useful to use the solutions to the basic hydrogen atom Hamiltonian to model these systems.

Definition 1.1.1. The **simple hydrogen atom Hamiltonian** is given by

$$\mathcal{H} = \underbrace{\frac{P_n^2}{2m_n}}_{\substack{\text{Nucleus} \\ \text{Kinetic Energy}}} + \underbrace{\frac{P_n^2}{2m_n}}_{\substack{\text{Electron} \\ \text{Kinetic Energy}}} - \underbrace{\frac{Ze^2}{4\pi\varepsilon_0|\vec{x_e} - \vec{x_n}|}}_{\substack{\text{Electrostatic} \\ \text{Potential}}} \tag{1.1.1}$$

This simplified Hamiltonian ignores relativity, spin, and magnetism.

Definition 1.1.2. Center of mass coordinates for the hydrogen atom are defined by

$$\vec{X} = \frac{m_e\vec{x_e} + m_n\vec{x_n}}{m_e + m_n} \quad \text{center of mass}$$
$$\vec{r} = \vec{x_e} - \vec{x_n} \quad \text{relative coordinate} \tag{1.1.2}$$

Corollary 1.1.3. The simple hydrogen atom Hamiltonian in center of mass coordinates is

$$\mathcal{H} = \underbrace{-\frac{\hbar}{2(m_e + m_n)}\nabla_X^2}_{\mathcal{H}_k} \underbrace{-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{4\pi\varepsilon_0|\vec{r}|}}_{\mathcal{H}_r} \tag{1.1.3}$$

Proposition 1.1.4. The Hamiltonians $\mathcal{H}_k$ and $\mathcal{H}_r$ are compatible observables.

$$[\mathcal{H}_k, \mathcal{H}_r] = 0, \quad [\mathcal{H}_k, \mathcal{H}] = 0, \quad [\mathcal{H}_r, \mathcal{H}] = 0 \tag{1.1.4}$$

Proposition 1.1.5. The Hamiltonian $\mathcal{H}_r$ can be further separated in terms of radial and angular dependence.

$$\mathcal{H}_r = \underbrace{\frac{\hbar^2 L^2}{2\mu|\vec{r}|^2}}_{\substack{\text{Tangential} \\ \text{Kinetic} \\ \text{Energy}}} - \underbrace{\frac{\hbar}{2\mu}\frac{P_r^2}{\hbar^2}}_{\substack{\text{Radial} \\ \text{Kinetic} \\ \text{Energy}}} - \underbrace{\frac{Ze^2}{4\pi\varepsilon_0|\vec{r}|}}_{\substack{\text{Electrostatic} \\ \text{Potential}}} \tag{1.1.5}$$

The solution to the Hamiltonian $\mathcal{H}_r$ can be written in terms of independent radial and angular components.

$$n = 1, 2, 3, 4, 5, \ldots$$
$$\ell = 0, 1, 2, 3, \ldots, n - 1 \tag{1.1.6}$$
$$m_\ell = -\ell, -\ell + 1, \ldots, -1, 0, 1, \ldots, \ell - 1, \ell$$

$$\psi_{n\ell m}(r, \theta, \phi) = U_n^\ell(r)Y_\ell^m(\theta, \phi) \tag{1.1.7}$$

Result 1.1.8. For the solution to the hydrogen atom $\psi_{n\ell m}(r, \theta, \phi)$, the following eigenvalue equations hold:

$$\mathcal{H}\psi_{n\ell m}(r, \theta, \phi) = -\frac{ZRyd}{n^2}\psi_{n\ell m}(r, \theta, \phi) \tag{1.1.8}$$

$$L^2\psi_{n\ell m}(r, \theta, \phi) = \ell(\ell + 1)\hbar^2\psi_{n\ell m}(r, \theta, \phi) \tag{1.1.9}$$

$$L_z\psi_{n\ell m}(r, \theta, \phi) = m\hbar\psi_{n\ell m}(r, \theta, \phi) \tag{1.1.10}$$

Definition 1.1.11. The **Bohr radius** is the average radius for the first energy level of the hydrogen atom given by

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu Z e^2} \tag{1.1.11}$$

Definition 1.1.12. The **Rydberg constant** is the first energy level of hydrogen given by

$$Ryd = \frac{\hbar^2}{2a_0^2\mu} = \frac{e^2}{8\pi\varepsilon_0 a_0} \tag{1.1.12}$$

Result 1.1.13. The **energy eigenvalues of hydrogen** are

$$E_n = -\frac{Z^2\hbar^2}{2a_0^2\mu}\frac{1}{n^2} = -\frac{Z^2\mathrm{Ryd}}{n^2} \tag{1.1.13}$$

1.1.14   Radial Component of Hydrogen

Definition 1.1.15. The **Laguerre polynomials** $L_q(z)$ are polynomials of degree q defined by

$$L_q(z) = e^z \frac{d^q}{dx^q}(z^q e^{-}z) \tag{1.1.15}$$

Definition 1.1.16. The **associated Laguerre polynomials** are polynomials of degree $q - p$ defined by

$$L_q^p(z) = \frac{d^p}{dx^p}L_q(x) \tag{1.1.16}$$

Result 1.1.17. The **radial component** $Y_\ell^m(\theta, \phi)$ has eigenvalues with eigenstates given by

$$U_n^\ell(r) = -\sqrt{\left(\frac{2Z}{na_0}\frac{(n-\ell-1)!}{2n\left[(n+\ell)!\right]^3}\right)^3} e^{-Zr/na_0}\left(\frac{2Zr}{na_0}\right)^\ell L_{n+\ell}^{2\ell+1}(2Zr/na_0) \tag{1.1.17}$$

1.1.18   Angular Component of Hydrogen

Definition 1.1.19. The **Legendre polynmials** denoted $P_\ell(z)$ are polynomials of degree ℓ that appear in spherically symmetric systems. They are defined with Rodrigues' formula given by

$$P_\ell(z) = \frac{1}{2^\ell \ell!}\frac{d^\ell}{dz^\ell}(z^2 - 1)^\ell \tag{1.1.19}$$

Definition 1.1.20. The **associated Legendre polynomials** denoted $P_\ell^m(z)$ are polynomials calculated from the Legendre polynomials. They are equivalently defined by the following formulas

$$\begin{aligned}
P_\ell^m(z) &= (-1)^m(1-z^2)^{m/2}\frac{d^m}{dz^m}P_\ell(z) \\
&= \frac{(-1)^m}{2^\ell \ell!}(1-z^2)^{m/2}\frac{d^{\ell+m}}{dz^{\ell+m}}(z^2-1)^\ell
\end{aligned} \tag{1.1.20}$$

Result 1.1.21. The **angular solution** $Y_\ell^m(\theta, \phi)$ has eigenvalues with eigenstates given by

$$Y_\ell^m(\theta, \phi) = (-1)^m\sqrt{\frac{2(\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}P_\ell^m(\cos\theta)e^{im\phi} \tag{1.1.21}$$

1.2 Electron Configurations

Theorem 1.2.1. The **Pauli exclusion principle** states that two or more identical particles cannot occupy the same state.

Theorem 1.2.2. Hund's rules state that electrons in a multi-electron atom fill shells according to the following rules.

1. Aligned Spins have lower energy. Maximize $S = \sum_i s_i$.

2. Minimized Electron Repulsions have lower energy. Maximize $L = \sum_i \ell_i$.

3. Shells fill according to the following pattern, $J = L - S$ when a shell is less that half full and $J = L + S$ when a shell is more than half full.

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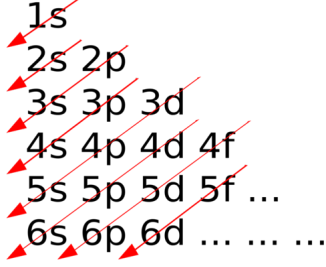
Definition 1.2.3. The **spectroscopic notation** for an electron configuration with total spin S, orbital angular momentum L and total angular momentum J is

$$^{2S+1}L_j \tag{1.2.3}$$

where L is replaced with letters S, P, D, F for $L = 0, 1, 2, 3$

1.2.4 Magnetism

Definition 1.2.5. Diamagnetism occurs when the total magnetic moment of an individual atom arranges opposite the direction of an applied field.

Definition 1.2.6. Paramagnetism occurs when the total magnetic moment of an individual atom arranges in the same direction of an applied field.

Definition 1.2.7. For a single atom with Hamiltonian H_0 and gyromagnetic factor $g \approx 2$ in an applied magnetic field $\vec{B}$ such that $\vec{\nabla} \times \vec{A} = \vec{B}$ the Hamiltonian of a single atom is

$$H = H_0 + \underbrace{\mu_B \vec{B}(\vec{\ell} + g\vec{S})}_{\text{Paramagnetism}} + \underbrace{\frac{e^2}{2m}\vec{A}^2}_{\text{Diamagnetism}} \tag{1.2.7}$$

Proposition 1.2.8. For individual atoms, if $J = 0$ diamagnetism will occur otherwise if $J \neq 0$ paramagnetism will occur.

Definition 1.2.9. Feromagnetism occurs when there is macroscopic permanent alignment of the magnetic moments of multiple atoms.

Definition 1.2.10. Anti-feromagnetism occurs when there is macroscopic permanent anti-alignment of the magnetic moments of multiple atoms.

1.3 Diatomic Molecules

Definition 1.3.1. The Hamiltonian for H_2 is

$$H = \underbrace{\frac{-\hbar}{2m_A}\nabla_A^2 - \frac{\hbar}{2m_B}\nabla_B^2}_{\text{Nuclei Kinetic Energy}} \underbrace{- \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2}_{\text{Electrons Kinetic Energy}} \underbrace{- \frac{Z_A e^2}{4\pi\varepsilon_0 r_{1A}} - \frac{Z_B e^2}{4\pi\varepsilon_0 r_{1B}} - \frac{Z_A e^2}{4\pi\varepsilon_0 r_{2A}} - \frac{Z_A e^2}{4\pi\varepsilon_0 r_{2B}}}_{\text{Nuclear-Electron Electrostatic Potential}} \underbrace{+ \frac{e^2}{4\pi\varepsilon_0 r_{12}}}_{\substack{\text{Nuclear-Nuclear} \\ \text{Electrostatic} \\ \text{Potential}}} \underbrace{\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R_{AB}}}_{\substack{\text{Electron-Electron} \\ \text{Electrostatic} \\ \text{Potential}}}$$
$$\tag{1.3.1}$$

Corollary 1.3.2. The Hamiltonian for H_2 in Hartree units is

$$H = \frac{1}{2m_A}\nabla_A^2 - \frac{1}{2m_B}\nabla_B^2 - \frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z_A}{r_{1A}} - \frac{Z_B}{r_{1B}} - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{2B}} + \frac{1}{r_{12}} + \frac{Z_A Z_B}{R_{AB}} \tag{1.3.2}$$

Proposition 1.3.3. The H_2 system cannot be solved due to the complexity of the electron-electron interaction.

1.3.4 Linear Combinations of Atomic Orbitals

Definition 1.3.5. The **linear combinations of atomic orbitals** approximation is a method for approximating diatomic molecules.

$$\psi \approx \frac{1}{\sqrt{2 \pm 2s}}(a(\vec{r}) \pm b(\vec{r})) \tag{1.3.5}$$

Definition 1.3.6. The **symmetric bond** written g (for garade) is the even linear combination

$$\psi_+ = \frac{1}{\sqrt{2 + 2s}}(a(\vec{r}) + b(\vec{r})) \tag{1.3.6}$$

Definition 1.3.7. The **antisymmetric bond** written u (for ungarade) is the odd linear combination

$$\psi_+ = \frac{1}{\sqrt{2 - 2s}}(a(\vec{r}) - b(\vec{r})) \tag{1.3.7}$$

Proposition 1.3.8. Symmetric bonds have an increased probability of electrons near both nuclei with strong binding. However, antisymmetric bonds have a decreased probability of electron near both nuclei with weak binding.

Definition 1.3.9. The **molecular orbital diagram** is a notation for linear combinations of atomic orbitals that represents the atom orbitals and the molecular orbitals.
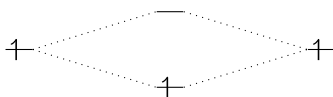
Definition 1.3.10. The **bond order** denoted B is defined as

$$B = \frac{[\# \text{ of bonding } e^-] - [\# \text{ of antibonding } e^-]}{2} \tag{1.3.10}$$

Corollary 1.3.11. A molecule will be stable if and only if $B > 0$.

Definition 1.3.12. For the s shell there are two bonding shells: the **s sigma bonding** shell is σ_g and the **s sigma antibonding** shell is σ_u^*. For the **p** shell there are 4 bonding shells: the **p sigma bonding** shell is σ_g, the **p sigma antibonding** shell is σ_u^*, the **p pi bonding shell** is π_u and the **p pi antibonding** shell is π_g^*.

Example. Consider diatomic Flourine: F_2. Fourine has electron configuration $1s^2 2s^2 2p^5$, so the molecular orbital diagram is
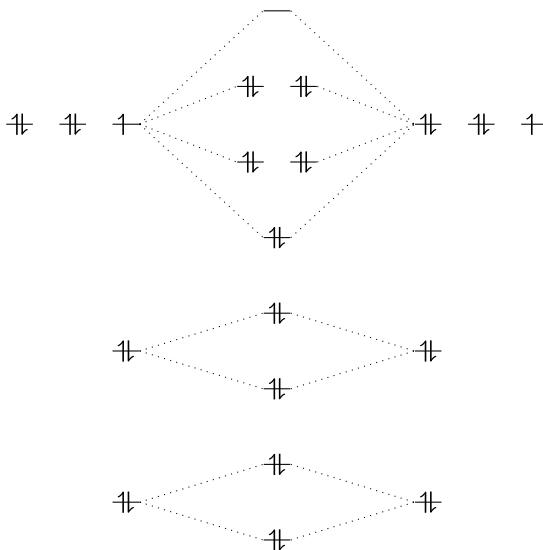
This

Definition 1.3.13. The **spectroscoptic notation** or **term symbols** for a molecular electron configuration with total spin S, orbital angular momentum L and total symmetry y is

$$^{2S+1}\Lambda_y \tag{1.3.13}$$

where Λ is replaced with symbols $\Sigma, \Pi, \Delta, \Phi$ for $L = 0, 1, 2, 3$ and $g \times g = g, u \times u = g, g \times u = u$.

Definition 1.3.14. The **Heitler-London Method** is a method of approximating molecular wavefunctions that uses LCAO but with the minor terms $H^- H^+$ terms dropped

$$\psi_{HL} = N(a(r_1)b(r_2) + b(r_1)a(r_2)) \tag{1.3.14}$$

Chapter 2

Crystal Structures

2.1 Lattice and Basis

Definition 2.1.1. A **crystal** is a periodic arrangement of atoms

Definition 2.1.2. A **lattice** is a set of points defined as integer sums of primitive lattice vectors.

Definition 2.1.3. The **primitive lattice vectors** of a lattice is a set of vectors that forms an integer basis for a lattice. Each primitive lattice vector must be integer linearly independent and the set of primitive lattices vectors must generate the set of lattice points.
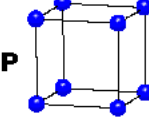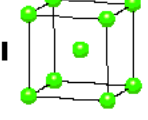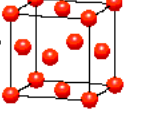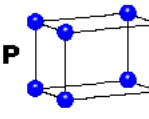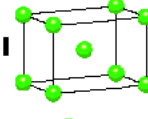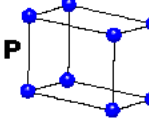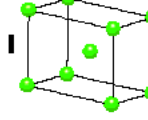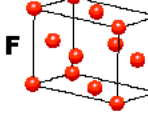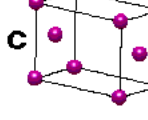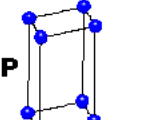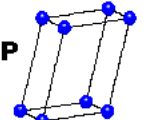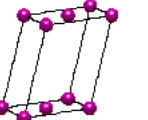
Definition 2.1.4. A set of vectors $\{\mathbf{v_1}, \mathbf{v_2}, \ldots, \mathbf{v_n}\}$ is **integer linearly independent** iff there does not exists non-zero integers $z_1, z_2, \ldots, x_n \in \mathbb{Z}$ such that

$$z_1\mathbf{v_1} + z_2\mathbf{v_2} + \cdots + z_n\mathbf{v_n} = \mathbf{0} \tag{2.1.4}$$

Definition 2.1.5. A set of vectors $\{\mathbf{v_1}, \mathbf{v_2}, \ldots, \mathbf{v_n}\}$ is **generating** iff for every lattice point $\mathbf{r}$ there exists unique integers $z_1, z_2, \ldots, x_n \in \mathbb{Z}$ such that

$$z_1\mathbf{v_1} + z_2\mathbf{v_2} + \cdots + z_n\mathbf{v_n} = \mathbf{r} \tag{2.1.5}$$

Theorem 2.1.6. The set of all possible lattices is classified by the following 14 Bravais lattices:

CUBIC
$a = b = c$
$\alpha = \beta = \gamma = 90°$

TETRAGONAL
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

ORTHORHOMBIC
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

HEXAGONAL
$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$

TRIGONAL
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

MONOCLINIC
$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$

TRICLINIC
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ **14 Bravais Lattices**

Proposition 2.1.7. A choice of lattice vectors is non unique.

Definition 2.1.8. A **basis** is a set of vectors that when repeated for every lattice points uniquely reproduces the entire lattice.

Theorem 2.1.9. Any crystal can be represented as a lattice and a basis.

Definition 2.1.10. A **unit cell** is a region of space which when repeated across a lattice completely reconstructs a crystal structure with no overlapping points.

Definition 2.1.11. A **primitive unit cell** is a unit cell with only one lattice point.