
CHEM 6634: Quantum Chemistry and Spectroscopy

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TR 11:00 AM - 12:15 PM

Room: Davidson 325

Instructor: Prof. Nick Mayhall, Davidson Hall 421C, nmayhall@vt.edu

Office Hours: 11:00 AM - 12:00 PM Wednesday.

Required Textbook: *Molecular Quantum Mechanics*: 5th edition, Atkins and Friedman,
ISBN 978-0-19-954142-3

Helpful textbooks:

- *Modern Quantum Chemistry*, Szabo and Ostlund;
- *Introduction to Computational Chemistry*, Jensen;
- *Quantum Mechanics*, Cohen-Tannoudji
- *Introduction to Quantum Mechanics in Chemistry*, Ratner, Schatz

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1 Math Review

1.1 Wavefunction space

- Schrödinger Equation for one particle:

$$i\hbar \frac{d}{dt} \Psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t) + V(\mathbf{r}, t) \Psi(\mathbf{r}, t) \quad (1)$$

$$= \hat{H} \Psi(\mathbf{r}, t) \quad (2)$$

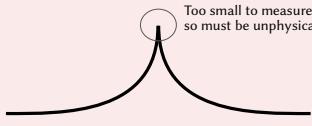
- Without justification: $\Psi(\mathbf{r}, t)$ is a probability amplitude with $|\Psi(\mathbf{r}, t)|^2 d^3r$ being the probability of finding the particle at time t inside d^3r about r .
- As a probability: $\int d^3\mathbf{r} |\Psi(\mathbf{r}, t)|^2 = 1$
 - thus, $\Psi(\mathbf{r}, t)$ is restricted in form
- Restrictions on functional form of $\Psi(\mathbf{r}, t)$:

Restrictions on functional form of $\Psi(\mathbf{r}, t)$, defining wavefunction space, \mathcal{F}

Square integrable \rightarrow set “ L^2 ” which has the structure of a Hilbert space (complete, and has inner product)

Continuous

Infinitely-differentiable: (any cusp would occur at a space scale which is beyond measurement, and thus cannot be physical, also, kinetic energy would blow up)



Bounded domain: system should be finite

- \mathcal{F} forms a vector space

$$\Psi_3 = \lambda_1 \Psi_1 + \lambda_2 \Psi_2 \in \mathcal{F} \quad (3)$$

- Familiar example: 3D space

- Any linear combination of \vec{x} , \vec{y} , and \vec{z} is also a vector in that space.

$$\vec{v} = v_x \vec{x} + v_y \vec{y} + v_z \vec{z} = \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix}_{xyz} \quad (4)$$

subscript “ xyz ” indicates that the vector is in the cartesian coordinate system

- This vector space has a **scalar product** (or **inner product** or “overlap”)

$$(\phi, \psi) = \int d^3 \mathbf{r} \phi(\mathbf{r})^* \psi(\mathbf{r}) < |\infty| \quad (5)$$

- Properties:

$$(\phi, \psi) = (\psi, \phi)^* \quad \text{complex conjugate} \quad (6)$$

$$(\phi, \lambda_1 \psi_1 + \lambda_2 \psi_2) = \lambda_1 (\phi, \psi_1) + \lambda_2 (\phi, \psi_2) \quad \text{linear wrt. } |\psi\rangle \quad (7)$$

$$(\lambda_1 \phi_1 + \lambda_2 \phi_2, \psi) = \lambda_1^* (\phi_1, \psi) + \lambda_2^* (\phi_2, \psi) \quad \text{antilinear or conjugate linear wrt. } |\phi\rangle \quad (8)$$

- Scalar product generalizes dot product of 3D vectors

$$(\vec{v}, \vec{w}) = \vec{v} \cdot \vec{w} = \vec{v}^\dagger \vec{w} = \sqrt{\vec{v} \cdot \vec{v}} \sqrt{\vec{w} \cdot \vec{w}} \cos \theta$$

Use $\cos \theta$ to illustrate Schwartz inequality

- **Schwarz inequality :**

$$|(\phi, \psi)| \leq \sqrt{(\phi, \phi)} \sqrt{(\psi, \psi)} \quad (9)$$

- **linear operator**

- operator: a transformation which maps one function onto another function
- for linear operator, \hat{A} , and number, a :

Properties of linear operators

$$\hat{A}\psi(r) = \psi(r)' \quad \text{operator definition}$$

$$\hat{A}(\psi(r) + \phi(r)) = \hat{A}\psi(r) + \hat{A}\phi(r) \quad \text{additivity}$$

$$\hat{A}(a\psi(r)) = a\hat{A}\psi(r) \quad \text{homogeneity}$$

- Examples:

- * Multiplication: $\hat{X}\psi = x\psi$
- * Differentiation: $\hat{D}_x\psi = \frac{d}{dx}\psi$
- * Exponentiation: $e^{\psi+\phi} \neq e^\psi + e^\phi$

- Order matters! : $\hat{A}\hat{B} \neq \hat{B}\hat{A}$

Example, consider an arbitrary function of x , $f(x)$:

$$x \frac{d}{dx} f(x) = xf(x)'$$

but reversing the order:

$$\frac{d}{dx} xf(x) = f(x) + xf(x)'$$

so, in general:

$$\frac{d}{dx} x \neq x \frac{d}{dx}$$

- commutator : $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

$$\left[\frac{d}{dx}, x \right] f(x) = \left(\frac{d}{dx}x - x \frac{d}{dx} \right) f(x) = f(x) + xf(x)' - f(x)' = f(x)$$

such that

$$\left[\frac{d}{dx}, x \right] = 1$$

reversing order inside commutator changes sign:

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}]$$

● Bases in \mathcal{F} : $\{u_i(r)\}$

- Just like \vec{x} , \vec{y} , and \vec{z} form a basis for 3D space, we can use bases for \mathcal{F}
- For convenience, $\{u_i(r)\}$ are typically orthonormal

$$(u_i, u_j) = \int u_i(r)^* u_j(r) d^3r = \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{else} \end{cases} \quad (10)$$

Where, δ_{ij} is the kronecker delta

- If $\{u_i(r)\}$ is a basis for \mathcal{F} it can be used to express any $\Psi(r)$

$$\Psi(r) = \sum_i u_i(r) c_i$$

- Coefficients are scalar products

$$(u_j(r), \Psi(r)) = \sum_i (u_j(r), u_i(r)) c_i \quad (11)$$

$$= \sum_i \delta_{ij} c_i \quad (12)$$

$$= c_j \quad (13)$$

- Scalar products using a basis: let $\phi(r) = \sum_j b_j u_j(r)$

$$(\phi, \psi) = \sum_i \sum_j (b_i u_i, c_j u_j) \quad (14)$$

$$= \sum_i \sum_j b_i^* c_j (u_i, u_j) \quad (15)$$

$$= \sum_i \sum_j b_i^* c_j \delta_{ij} \quad (16)$$

$$= \sum_i b_i^* c_i \quad (17)$$

$$(\psi, \psi) = \sum_i c_i^* c_i = \sum_i |c_i|^2 \geq 0 \quad (18)$$

- Completeness of $\{u_i(r)\}$:

* $\{u_i\}$ must span the space of \mathcal{F}

$$\psi(r) = \sum_i c_i u_i(r) = \sum_i (u_i, \psi) u_i(r) \quad (19)$$

$$= \sum_i \left[\int u_i^*(r') \psi(r') d^3 r' \right] u_i(r) \quad \text{expand scalar product as integral} \quad (20)$$

$$= \int \left[\sum_i u_i^*(r') u_i(r) \right] \psi(r') d^3 r' \quad \text{bring summation into integral} \quad (21)$$

$$= \int [f(r, r')] \psi(r') d^3 r' \quad \text{introduce some function, } f \quad (22)$$

* For this to equality to hold, the following must be true:

$$\sum_i u_i^*(r') u_i(r) = \delta(r - r') \quad \text{closure relation} \quad (23)$$

* Where we have introduced the Dirac delta function:

$$\delta(r - r') = \begin{cases} +\infty & \text{if } r = r' \\ 0 & \text{else} \end{cases} \quad (24)$$

which has the following property:

$$\int_{-\infty}^{+\infty} \delta(r - r') dr' = 1 \quad \text{continuous analogy of } \delta_{ij} \quad (25)$$

Start of Lecture 2

- Generalization to continuous bases:

- Essentially, $\sum_i \rightarrow \int d\alpha$ and $c_i \rightarrow c(\alpha)$

Relation	Discrete: index i	Continuous, index α
Orthonormalization	$(u_i(r), u_j(r)) = \delta_{ij}$	$(u_\alpha(r), u_{\alpha'}(r)) = \delta(\alpha - \alpha')$
Closure	$\sum_i u_i(r) u_i(r')^* = \delta(r - r')$	$\int_\alpha u_\alpha(r) u_\alpha(r')^* d\alpha = \delta(r - r')$
Expansion	$\psi(r) = \sum_i c_i u_i(r)$	$\psi(r) = \int_\alpha c(\alpha) u_\alpha(r) d\alpha$
Coefficients	$c_i = (u_i, \psi)$	$c(\alpha) = (u_\alpha, \psi)$
Scalar product	$(\phi, \psi) = \sum_i b_i^* c_i$	$(\phi, \psi) = \int_\alpha b(\alpha)^* c(\alpha) d\alpha$

- Example, 1D plane waves:

$$\nu_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} \quad (26)$$

- Apply the closure relation for a continuous basis:

$$\psi(x) = \int dx' \delta(x - x') \psi(x') \quad (27)$$

$$= \int dx' \left(\int dp v_p^*(x') v_p(x) \right) \psi(x') \quad (28)$$

$$= \int dp v_p(x) \left(\int dx' v_p^*(x') \psi(x') \right) \quad (29)$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int dp e^{ipx/\hbar} \bar{\psi}(p) \quad (30)$$

such that $\psi(x)$ is written as the Fourier transform of $\bar{\psi}(p)$, which itself is the inverse Fourier transform of $\psi(x)$,

$$\bar{\psi}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int dx' e^{-ipx'/\hbar} \psi(x') \quad (31)$$

Equivalently, $\bar{\psi}(p)$ also happens to be the “expansion coefficients” in the plane-wave basis

$$\bar{\psi}(p) = (\nu_p(x), \psi(x)) \quad (32)$$

$$= \int_{-\infty}^{+\infty} dx \nu_p(x)^* \psi(x) \quad (33)$$

$$= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{+\infty} dx \psi(x) e^{-ipx/\hbar} \quad (34)$$

1.2 State Space and Dirac Notation

- Once a basis is chosen, $\Psi(r)$ can be fully described by a vector of coefficients

Basis	Components
$u_i(r)$	c_i
$u_\alpha(r)$	$c(\alpha)$
:	:

- the components of the $\Psi(r)$ change depending on the basis

Assume $\{\vec{x}', \vec{y}', \vec{z}'\}$ is rotated w.r.t. $\{\vec{x}, \vec{y}, \vec{z}\}$

$$\vec{v} = \begin{pmatrix} v_{x'} \\ v_{y'} \\ v_{z'} \end{pmatrix}_{x'y'z'} = \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix}_{xyz}$$

but

$$v_{x'} \neq v_x$$

- In fact, $\Psi(r)$ itself can be thought of as a coefficient of an abstract wavefunction (without any basis). $\Psi(r)$ is thus the representation of the state “ Ψ ” in a continuous basis in real space, $u_{r_0}(r) = \delta(r - r_0)$.

$$\Psi(r) = \int dr_0 \delta(r - r_0) \Psi(r_0) \quad (35)$$

- To better articulate this, let's adopt a notation which is “basis agnostic” → Dirac notation
- For every state, there exists a state vector called a ket, $|\rangle$
 - $|\rangle$ fully specifies the state of the system, without referring to a basis
- $|\psi\rangle$ is a vector corresponding to $\psi(r)$, which lives in a vector space, \mathcal{E} , called state space
- \mathcal{F} is isomorphic to \mathcal{E}
- Dual space, \mathcal{E}^*

- Linear functional: $\chi(|\psi\rangle) \rightarrow k \in \mathbb{C}$

function	$\xrightarrow{\text{operator}}$	function
function	$\xrightarrow{\text{functional}}$	number

- The set of all linear functionals defined on $|\psi\rangle \in \mathcal{E}$ constitutes a vector space, called **dual space**
- A vector in this dual space is called a **bra**, $\langle |$

$$\chi(|\psi\rangle) = \langle \chi | \psi \rangle = k \in \mathbb{C} \quad \langle \chi | \in \mathcal{E}^* \quad (36)$$

- For finite dimensions, \mathcal{E}^* and \mathcal{E} are isomorphic.
 - * each ket has an associated bra, but not all possible bra's must have an associated ket
 - * we won't consider this further
- To every $|\psi\rangle$, there corresponds one $\langle \psi |$
- Each linear functional, $\langle \phi |$, transforms $|\psi\rangle$ into the scalar product of $|\phi\rangle$ and $|\psi\rangle$

$$\langle \phi | \psi \rangle = (|\phi\rangle, |\psi\rangle) = k \in \mathbb{C} \quad (37)$$

$$\Leftrightarrow \int \phi(r)^* \psi(r) d^3r \quad (38)$$

1.2.1 Linear Operators with Dirac Notation

- bra-ket = $\langle \phi | \psi \rangle = k \in \mathbb{C}$
- ket-bra? : Consider action on arbitrary function

$$(|\psi\rangle\langle\phi|) |\chi\rangle = |\psi\rangle \langle \phi | \chi \rangle \quad (39)$$

$$= |\psi\rangle k \quad (40)$$

- thus $|\psi\rangle\langle\phi|$ is an operator
- Order of bras and kets is everything!

$\langle \psi \phi \rangle$	= complex number
$ \psi\rangle\langle\phi $	operator

- Analogy with 3-space vectors

- basis vectors

$$\vec{e}_i = \{\vec{x}, \vec{y}, \vec{z}\} = \left\{ \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \right\} \quad (41)$$

$$\langle x|x \rangle = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = 1 \quad (42)$$

$$\langle x|y \rangle = \begin{pmatrix} 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = 0 \quad (43)$$

$$|x\rangle\langle y| = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (44)$$

In a given basis, kets are column vectors, and operators are matrices!

- Projector onto $|\psi\rangle$

- assume $|\psi\rangle$ is normalized, $\langle\psi|\psi\rangle = 1$
- define $\hat{P}_\psi = |\psi\rangle\langle\psi|$

$$\hat{P}_\psi |\phi\rangle = |\psi\rangle \langle\psi|\phi\rangle \propto |\psi\rangle \quad (45)$$

- proportionality constant = overlap
- this is called an **orthogonal projection**

- Projections are **idempotent** : i.e., $\hat{P}\hat{P} = \hat{P}$

$$|\psi\rangle\langle\psi| |\psi\rangle\langle\psi| = |\psi\rangle (\langle\psi|\psi\rangle) \langle\psi| = |\psi\rangle\langle\psi| \quad \text{since normalized} \quad (46)$$

- Resolution of the Identity : $\sum_i |\psi_i\rangle\langle\psi_i| = \mathbf{I}$

$$|x\rangle\langle x| + |y\rangle\langle y| + |z\rangle\langle z| = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (47)$$

$$= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (48)$$

$$= \mathbf{I} \quad (49)$$

- subspace projections

Project cartesian 3D vector, $|v\rangle$, onto x, y plane.

$$\hat{P}_{xy} = |x\rangle\langle x| + |y\rangle\langle y| = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (50)$$

$$\hat{P}_{xy} |v\rangle = (|x\rangle\langle x| + |y\rangle\langle y|) (v_x |x\rangle + v_y |y\rangle + v_z |z\rangle) \quad (51)$$

$$= v_x |x\rangle + v_y |y\rangle \quad (52)$$

$$= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix} = \begin{pmatrix} v_x \\ v_y \\ 0 \end{pmatrix} \quad (53)$$

Hartree-Fock density matrix is a subspace projection operator. It is a projection onto the occupied space.

- matrix representation of operators

$$\hat{A} = \mathbf{I} \hat{A} \mathbf{I} = \sum_{ij} |\psi_i\rangle\langle\psi_i| \hat{A} |\psi_j\rangle\langle\psi_j| \quad \text{Use RI} \quad (54)$$

$$= \sum_{ij} |\psi_i\rangle A_{ij} \langle\psi_j| \quad \text{matrix elements} \quad (55)$$

- A_{ij} is the i, j^{th} element of the matrix representation of \hat{A} in the basis $\{\psi_i\}$
- since \hat{A} is an operator, $\hat{A}|\psi\rangle = |\psi'\rangle$

$$\langle\psi_i| \hat{A} |\psi_j\rangle = \langle\psi_i| \psi'_j \rangle \quad \text{scalar product - we know what to do} \quad (56)$$

$$\Leftrightarrow \int \psi_i^*(r) \hat{A} \psi_j(r) d^3r \quad \text{if position space representation} \quad (57)$$

- What about $\hat{A}\hat{B}$?

$$\hat{A}\hat{B} = \mathbf{I} \hat{A} \mathbf{I} \hat{B} \mathbf{I} \quad (58)$$

$$= \sum_{ijk} |u_i\rangle\langle u_i| \hat{A} |u_j\rangle\langle u_j| \hat{B} |u_k\rangle\langle u_k| \quad (59)$$

$$= \sum_{ijk} |u_i\rangle A_{ij} B_{jk} \langle u_k| \quad (60)$$

$$\langle u_i| \hat{A}\hat{B} |u_k\rangle = (\hat{A}\hat{B})_{ik} = A_{ij} B_{jk} \quad (61)$$

Start of Lecture 3

- adjoint or Hermitian conjugate

$ \psi\rangle \xrightarrow{\hat{A}} \psi'\rangle$ $\Downarrow \quad \Downarrow \quad \Downarrow$ $\langle\psi \xrightarrow{\hat{A}^\dagger} \langle\psi' $	$\hat{A} \psi\rangle = \psi'\rangle$ Adjoint $\langle\psi \hat{A}^\dagger = \langle\psi' $
--	---

Adjoint “ † ” is the operation which formally establishes the one-to-one relationship between bras and kets.

Order changes

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger \quad (62)$$

$$(|x\rangle\langle y|)^\dagger = (\langle y|)^\dagger (|x\rangle)^\dagger \quad \text{Example} \quad (63)$$

$$= |y\rangle\langle x| \quad (64)$$

$$= \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}^\dagger = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{If real, adjoint = transpose} \quad (65)$$

$$(\hat{A}^\dagger)_{ij} = (\hat{A})_{ji}^* \quad (66)$$

To obtain Hermitian conjugate:

1. Replace:

- $\lambda \rightarrow \lambda^*$ for $\lambda \in \mathbb{C}$
- $|\psi\rangle \rightarrow \langle\psi|$
- $\langle\psi| \rightarrow |\psi\rangle$
- $\hat{A} \rightarrow \hat{A}^\dagger$

2. Reverse the order

- If $\hat{A}^\dagger = \hat{A}$, \hat{A} is said to be **Hermitian**.

1.3 Representations in the state space

- Choosing an orthonormal basis in state space, is called choosing a **representation**.
- Introduction of a basis, $\{|u_i\rangle\}$:

$$|\psi\rangle = \mathbf{I}|\psi\rangle \quad (67)$$

$$= \sum_i |u_i\rangle\langle u_i| |\psi\rangle \quad (68)$$

$$= \sum_i c_i |u_i\rangle \quad (69)$$

- Change of basis, $\{|u_i\rangle\} \rightarrow \{|w_j\rangle\}$:

$$|\psi\rangle = \sum_i |u_i\rangle c_i \quad (70)$$

$$= \sum_i \mathbf{I} |u_i\rangle c_i \quad (71)$$

$$= \sum_i \sum_j |w_j\rangle \langle w_j| u_i \rangle c_i \quad (72)$$

$$= \sum_i \sum_j |w_j\rangle S_{ji} c_i \quad (73)$$

get components in new basis, b_k :

$$b_k = \langle w_k | \psi \rangle \quad (74)$$

$$= \sum_i \langle w_k | u_i \rangle \langle u_i | \psi \rangle \quad (75)$$

$$= \sum_i S_{ki} c_i \quad (76)$$

- For change of basis: $\{|u_i\rangle\} \rightarrow \{|w_j\rangle\}$:

$$S_{ki} = \langle w_k | u_i \rangle \quad \text{Overlap, or scalar product} \quad (77)$$

$$S_{ik}^* = \langle u_i | w_k \rangle \quad \text{adjoint} \quad (78)$$

$$\sum_k S_{ik}^* S_{kj} = \sum_k \langle u_i | w_k \rangle \langle w_k | u_j \rangle \quad \text{Matrix multiply of both} \quad (79)$$

$$= \langle u_i | u_j \rangle \quad (80)$$

$$= \delta_{ij} \quad \text{Orthogonalization} \quad (81)$$

thus,

$$\mathbf{S} \mathbf{S}^\dagger = \mathbf{S}^\dagger \mathbf{S} = \mathbf{I} \quad (82)$$

$$\mathbf{S}^\dagger = \mathbf{S}^{-1} \quad S \text{ is thus a unitary matrix} \quad (83)$$

1.4 Eigenvalue equations and observables

1.4.1 Eigenvalue equations

- For $\lambda \in \mathbb{C}$, if

$$\hat{A} |\psi\rangle = \lambda |\psi\rangle \quad (84)$$

Then $|\psi\rangle$ is said to be an eigenvector of operator \hat{A} , with eigenvalue λ .

- An operator will (in general) have many eigenvalues:

$$\hat{A} |\psi_s\rangle = \lambda_s |\psi_s\rangle \quad (85)$$

- If each λ_s corresponds to a single $|\psi_s\rangle$, we say that λ_s is **non-degenerate**
- The number of linearly-independant eigenvectors associated with λ_i is the **order of degeneracy**, g_s
- Finding eigenvalues:

$$\langle u_i | \hat{A} | \psi_s \rangle = \lambda_s \langle u_i | \psi_s \rangle \quad \text{project onto some basis} \quad (86)$$

$$\sum_j \langle u_i | \hat{A} | u_j \rangle \langle u_j | \psi_s \rangle = \sum_j \lambda_s \langle u_i | u_j \rangle \langle u_j | \psi_s \rangle \quad \text{RI} \quad (87)$$

$$\sum_j A_{ij} c_{js} = \lambda_s c_{is} \quad (88)$$

$$\mathbf{A} \mathbf{c}_s = \mathbf{c}_s \lambda_s \quad \text{matrix form} \quad (89)$$

$$(\mathbf{A} - \mathbf{I} \lambda_s) \mathbf{c}_s = \mathbf{0} \quad (90)$$

- obviously, $\mathbf{c}_s = \mathbf{0}$ is a trivial (yet unphysical) solution.
- if $(\mathbf{A} - \mathbf{I} \lambda_s)^{-1}$ exists, then \mathbf{c}_s is trivial
- thus we want values of λ_s for which $(\mathbf{A} - \mathbf{I} \lambda_s)^{-1}$ does not exist
- equivalent to solving

$$|\mathbf{A} - \mathbf{I} \lambda_s| = 0 \quad \text{called the secular equation} \quad (91)$$

Examples:

$$\hat{A} = \frac{d}{dx} \quad (92)$$

$$|\psi\rangle = a e^{bx} \quad (93)$$

$$\frac{d}{dx} (a e^{bx}) = b (a e^{bx}) \quad (94)$$

$$\hat{A} = \frac{d^2}{dx^2} \quad (95)$$

$$|\psi\rangle = a \sin bx \quad (96)$$

$$\frac{d^2}{dx^2} (a \sin bx) = -b^2 (a \sin bx) \quad (97)$$

1.4.2 Hermitian operators

- Observables (or “measurable” quantities) are associated with a Hermitian operator
- Properties of **Hermitian** operators: $\hat{A}^\dagger = \hat{A}$
 1. Hermitian operators have real eigenvalues

$$\langle \lambda | \hat{A}^\dagger = \langle \lambda | \lambda^* \quad \text{take adjoint}$$

$$\langle \lambda | \hat{A} | \lambda \rangle = \lambda \quad \text{left multiply by } \langle \psi |$$

$$\langle \lambda | \hat{A}^\dagger | \lambda \rangle = \lambda^* \quad \text{right multiply by } |\psi \rangle$$

Since $\langle \lambda | \hat{A} | \lambda \rangle = \langle \lambda | \hat{A}^\dagger | \lambda \rangle$ definition of Hermitian
 then $\lambda = \lambda^*$ ■

2. Eigenvectors with different eigenvalues are orthogonal

$$\hat{A} |\lambda\rangle = \lambda |\lambda\rangle \quad \text{given}$$

$\langle \lambda' | \hat{A} = \lambda' \langle \lambda' |$ Since \hat{A} is Hermitian

$$\begin{aligned} \langle \lambda' | \hat{A} | \lambda \rangle &= \lambda \langle \lambda' | \lambda \rangle && \text{left multiply by } \langle \lambda' | \\ \langle \lambda' | \hat{A} | \lambda \rangle &= \lambda' \langle \lambda' | \lambda \rangle && \text{right multiply by } | \lambda \rangle \end{aligned}$$

$$(\lambda' - \lambda) \langle \lambda' | \lambda \rangle = 0 \quad \text{subtracting the two equations}$$

Thus, either $\lambda = \lambda'$ or $|\lambda\rangle$ and $|\lambda'\rangle$ are orthogonal ■

3. Linear combinations of e'vectors with same e'values can also be e'vectors, with same e'value.

$$\hat{A} |\lambda\rangle = \lambda |\lambda\rangle \quad \text{given}$$

$$\begin{aligned}\hat{A}(a|\lambda\rangle + b|\lambda'\rangle) &= a\hat{A}|\lambda\rangle + b\hat{A}|\lambda'\rangle && \text{linear operator} \\ &= a\lambda|\lambda\rangle + b\lambda'|\lambda'\rangle && \text{eigenvalues} \\ &= \lambda(a|\lambda\rangle + b|\lambda'\rangle)\end{aligned}$$

Since they can be combined, they can be orthogonalized, and thus form a basis for the space - the eigenbasis

Start of Lecture 4

1.4.3 Sets of commuting Hermitian operators

- If there exists a basis of eigenvectors common to \hat{A} and \hat{B} , these two operators commute

$$\begin{aligned}
 \hat{A} |\lambda_i\rangle &= a_i |\lambda_i\rangle && \text{given} \\
 \hat{B} |\lambda_i\rangle &= b_i |\lambda_i\rangle && \text{given} \\
 \\
 \hat{A}\hat{B} &= \hat{A} \sum_i |\lambda_i\rangle\langle\lambda_i| \hat{B} && \text{RI} \\
 &= \sum_i a_i |\lambda_i\rangle\langle\lambda_i| b_i && \text{eigenvalue definition} \\
 &= \sum_i b_i |\lambda_i\rangle\langle\lambda_i| a_i && \text{scalars commute} \\
 &= \hat{B} \sum_i |\lambda_i\rangle\langle\lambda_i| \hat{A} && \text{e'val definition} \\
 &= \hat{B}\hat{A} && \blacksquare
 \end{aligned}$$

- Theorems:

1. If $[\hat{A}, \hat{B}] = 0$, and if $\hat{A} |\lambda\rangle = \lambda |\lambda\rangle$,
then, $\hat{B} |\lambda\rangle$ is also an eigenvector of \hat{A} with eigenvalue λ .

$$\hat{B}\hat{A} |\lambda\rangle = \hat{B}\lambda |\lambda\rangle \quad \text{left multiply by } \hat{B} \quad (98)$$

$$\hat{A}\hat{B} |\lambda\rangle = \lambda \hat{B} |\lambda\rangle \quad \text{since they commute} \quad (99)$$

2. If $[\hat{A}, \hat{B}] = 0$, and if $\hat{A} |\lambda\rangle = \lambda |\lambda\rangle$ and $\hat{A} |\lambda'\rangle = \lambda' |\lambda'\rangle$ where $\lambda \neq \lambda'$,
then, $\langle\lambda| \hat{B} |\lambda'\rangle = 0$

$$\langle\psi_1| (\hat{A}\hat{B} - \hat{B}\hat{A}) |\psi_2\rangle = 0 \quad \text{Since } [\hat{A}, \hat{B}] = 0 \quad (100)$$

$$\langle\psi_1| \hat{A}\hat{B} |\psi_2\rangle - \langle\psi_1| \hat{B}\hat{A} |\psi_2\rangle = 0 \quad (101)$$

$$a_1 \langle\psi_1| \hat{B} |\psi_2\rangle - a_2 \langle\psi_1| \hat{B} |\psi_2\rangle = 0 \quad a_1 \text{ is real because Hermitian} \quad (102)$$

$$(a_1 - a_2) \langle\psi_1| \hat{B} |\psi_2\rangle = 0 \quad (103)$$

3. If $[\hat{A}, \hat{B}] = 0$,
then, the eigenvectors common to \hat{A} and \hat{B} can be used to construct an orthonormal basis for state space.

Degenerate eigenvectors of \hat{A} are not necessarily eigenvectors of \hat{B} , but it is possible to choose a linear combination of these vectors which are common eigenvectors to \hat{A} and \hat{B}

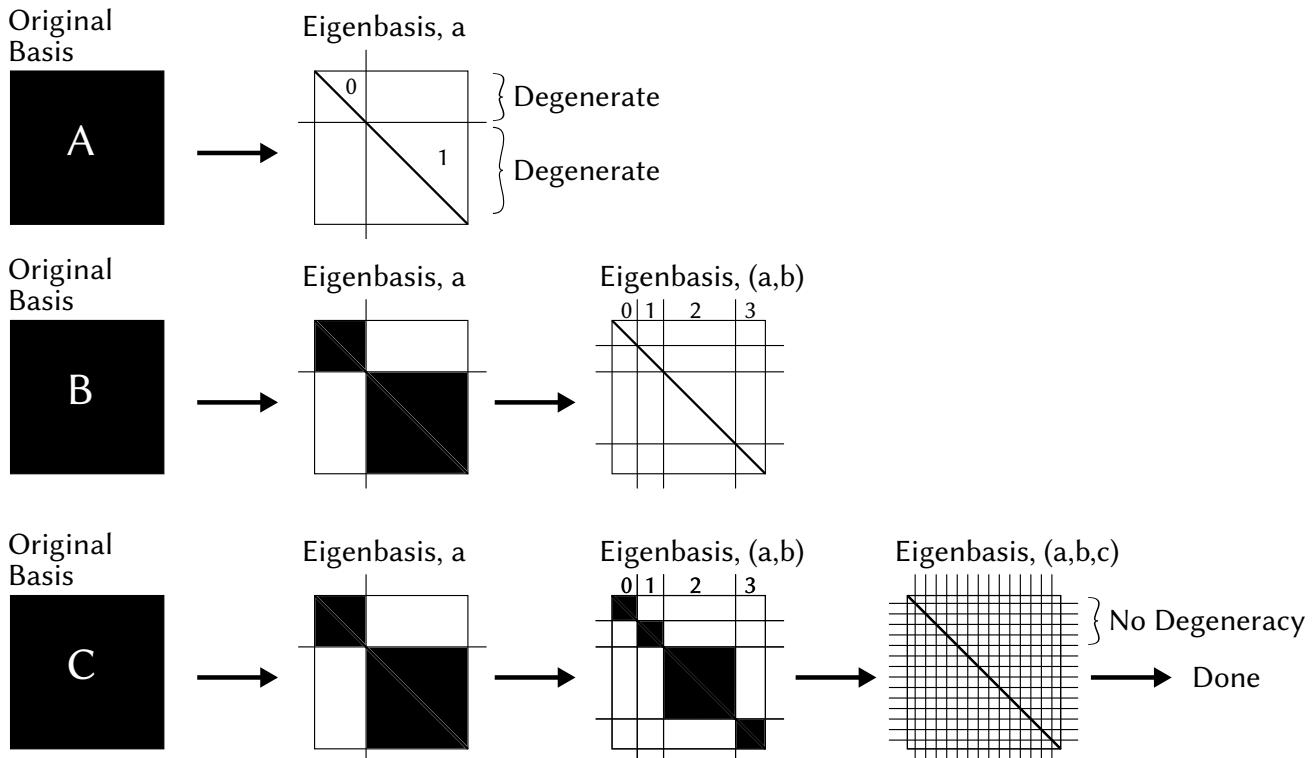
- Complete sets of commuting observables or (CSCO)

- If any eigenvalues of \hat{A} are degenerate, specifying the eigenvalue does not uniquely identify an eigenvector, but an eigensubspace
- A second commuting operator might be chosen which has distinct eigenvalues in that same eigensubspace

Definition: Complete sets of commuting observables

a set of commuting operators whose eigenvalues completely specify the state of a system

or a minimal set of commuting operators for which a list of eigenvalues (one for each operator in the set) identifies a specific vector



1.5 Two special representations, $\{|r\rangle\}$ and $\{|p\rangle\}$

- Let's consider two possible bases for \mathcal{F} :

$$\chi_{r_0}(r) = \delta(r - r_0) \Leftrightarrow |r_0\rangle \quad (104)$$

$$\nu_{p_0}(r) = \left(\frac{1}{2\pi\hbar}\right)^{3/2} e^{\frac{i}{\hbar} p_0 \cdot r} \Leftrightarrow |p_0\rangle \quad (105)$$

- Neither of these functions are members of \mathcal{F} , but it's ok
- Referred to as position and momentum functions

Note: 3D plane waves are just product of 1D plane waves

$$\begin{aligned} \nu_p(r) &= (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar} (p_x \vec{x} + p_y \vec{y} + p_z \vec{z}) \cdot (x \vec{x} + y \vec{y} + z \vec{z})} \\ &= (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar} p_x x} e^{\frac{i}{\hbar} p_y y} e^{\frac{i}{\hbar} p_z z} \\ &= (2\pi\hbar)^{-1/2} e^{\frac{i}{\hbar} p_x x} (2\pi\hbar)^{-1/2} e^{\frac{i}{\hbar} p_y y} (2\pi\hbar)^{-1/2} e^{\frac{i}{\hbar} p_z z} \\ &= \nu_{p_x}(x) \nu_{p_y}(y) \nu_{p_z}(z) \end{aligned}$$

- Orthonormalization:

$$\langle r_0 | r'_0 \rangle = \int dr \delta(r - r_0) \delta(r - r'_0) \quad (106)$$

$$= \delta(r_0 - r'_0) \quad \checkmark \quad (107)$$

(108)

$$\langle p_0 | p'_0 \rangle = \int dr \left(\frac{1}{2\pi\hbar}\right)^3 e^{\frac{-i}{\hbar} p_0 \cdot r} e^{\frac{i}{\hbar} p'_0 \cdot r} \quad (109)$$

$$= \int dr \left(\frac{1}{2\pi\hbar}\right)^3 e^{\frac{i}{\hbar} (p_0 - p'_0) \cdot r} \quad (110)$$

$$= \delta(p_0 - p'_0) \quad \text{trust me, or not!} \quad (111)$$

Use the following identity of the Fourier transform (typical for Quantum Mechanics):

$$\delta(x - x_0) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar} p_x (x - x_0)} dp_x$$

- Closure relation:

$$\int dr_0 |r_0\rangle \langle r_0| = \int dp_0 |p_0\rangle \langle p_0| = \mathbf{I}$$

- consider action on arbitrary function, $v(r) \Leftrightarrow |v\rangle$:

$$\begin{aligned}
 \left[\int dr_0 |r_0\rangle\langle r_0| \right] |v\rangle &= \int dr_0 |r_0\rangle \langle r_0| v \\
 &= \int dr_0 \delta(r - r_0) \int dr' \delta(r' - r_0) v(r') && \text{closure def} \\
 &= \int dr_0 \delta(r - r_0) v(r_0) && \text{use orthonormality} \\
 &= v(r) \\
 &\Leftrightarrow |v\rangle && \text{function is left unchanged}
 \end{aligned}$$

- thus, identity!
- Same for $|p_0\rangle$

- Therefore, $\{|r_0\rangle\}$ and $\{|p_0\rangle\}$ can form a basis for any function

- Express $|\psi\rangle$ in basis: $|r_0\rangle$

$$|\psi\rangle = \int dr_0 |r_0\rangle\langle r_0| |\psi\rangle \quad \text{RI} \quad (112)$$

$$= \int dr_0 \chi_{r_0}(r') \left[\int dr \chi_{r_0}(r)^* \psi(r) \right] \quad \text{Scalar product definition} \quad (113)$$

$$= \int dr_0 \chi_{r_0}(r') \left[\int dr \delta(r - r_0) \psi(r) \right] \quad \chi_{r_0}(r) \text{definition} \quad (114)$$

$$= \int dr_0 \chi_{r_0}(r') \psi(r_0) \quad (115)$$

- $\psi(r_0)$ is thus, the **wavefunction**, the state ket, $|\psi\rangle$, projected onto the position basis!
- What about $\{|p_0\rangle\}$?

$$|\psi\rangle = \int dp_0 |p_0\rangle\langle p_0| |\psi\rangle \quad \text{RI} \quad (116)$$

$$= \int dp_0 \nu_{p_0}(r') \left[\int dr \nu_{p_0}(r)^* \psi(r) \right] \quad \text{Scalar product definition} \quad (117)$$

$$= \int dp_0 \nu_{p_0}(r') \left[\int dr \left(\frac{1}{2\pi\hbar} \right)^{3/2} e^{\frac{-i}{\hbar} p_0 \cdot r} \psi(r) \right] \quad \nu_{p_0}(r) \text{definition} \quad (118)$$

$$= \int dp_0 \nu_{p_0}(r') \bar{\psi}(p_0) \quad \text{Fourier transform} \quad (119)$$

- Thus, in the $|p_0\rangle$ representation, the state ket, $|\psi\rangle$, is fully described by the “expansion coefficients” $\bar{\psi}(p_0)$, which is the Fourier transform of the wavefunction

Definition of the wavefunction:

$$\psi(r_0) = \langle r_0 | \psi \rangle$$

$$\bar{\psi}(p_0) = \langle p_0 | \psi \rangle$$

Start of Lecture 5

- Change of basis from $|r_0\rangle$ to $|p_0\rangle$

$$\begin{aligned}
 \psi(r_0) &= \langle r_0 | \psi \rangle && \text{wavefunction} \\
 &= \int dp_0 \langle r_0 | p_0 \rangle \langle p_0 | \psi \rangle && \text{RI} \\
 &= \int dp_0 \langle r_0 | p_0 \rangle \bar{\psi}(p_0) && \text{from above}
 \end{aligned}$$

where,

$$\begin{aligned}
 \langle r_0 | p_0 \rangle &= \int dr \chi_{r_0}(r) v_{p_0}(r) && \text{scalar product} \\
 \langle r_0 | p_0 \rangle &= (2\pi\hbar)^{-3/2} \int dr \delta(r - r_0) e^{\frac{i}{\hbar} p_0 \cdot r} && \text{function definitions} \\
 \langle r_0 | p_0 \rangle &= (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar} p_0 \cdot r_0} && \text{delta kills } r
 \end{aligned}$$

Combining these last two results:

$$\psi(r_0) = \int (2\pi\hbar)^{-3/2} e^{\frac{i}{\hbar} p_0 \cdot r_0} \bar{\psi}(p_0) dp_0$$

Thus,

$$\psi(r_0) \xleftarrow{\text{Fourier transform}} \bar{\psi}(p_0)$$

- Position and momentum operators

- In position representation, the position operator is just multiplication

$$\langle r_0 | \hat{X} | \psi \rangle = x \langle r_0 | \psi \rangle = x\psi(r_0)$$

- In momentum representation, the momentum operator is just multiplication

$$\langle p_0 | \hat{P}_x | \psi \rangle = p_x \langle p_0 | \psi \rangle = p_x \bar{\psi}(p_0)$$

- What about the position operator in the momentum basis?

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar} p_x \cdot x} \bar{\psi}(p_x) dp_x \quad \text{Defined above} \quad (120)$$

$$x\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} x e^{\frac{i}{\hbar} p_x \cdot x} \bar{\psi}(p_x) dp_x \quad \text{multiply by } x \quad (121)$$

$$uv - \int u dv = \int v du \quad \text{integration by parts} \quad (122)$$

$$u = -i\hbar e^{\frac{i}{\hbar}px} \quad v = \bar{\psi}(p_x)$$

$$du = xe^{\frac{i}{\hbar}px} dp \quad dv = \frac{\partial}{\partial p_x} \bar{\psi}(p_x) dp_x$$

$$x\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \left[-i\hbar e^{\frac{i}{\hbar}px} \bar{\psi}(p_x) + \int i\hbar e^{\frac{i}{\hbar}px} \frac{\partial}{\partial p_x} \bar{\psi}(p_x) dp_x \right]_{-\infty}^{\infty} \quad \text{substitute} \quad (123)$$

$$x\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} i\hbar e^{\frac{i}{\hbar}px} \frac{\partial}{\partial p_x} \bar{\psi}(p_x) dp_x \quad \text{wavefunction integrable} \quad (124)$$

Comparing the equations for $x\psi(x)$, one sees that $x \rightarrow i\hbar \frac{\partial}{\partial p_x}$ ■

- This is a better derivation:

Start with,

$$\begin{aligned} \langle p_0 | \hat{X} | \psi \rangle &= \int_{-\infty}^{\infty} dx_0 \langle p_0 | x_0 \rangle \langle x_0 | \hat{X} | \psi \rangle && \text{RI} \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx_0 \left(\int_{-\infty}^{\infty} dx e^{-ip_0x/\hbar} \delta(x - x_0)x \right) \langle x_0 | \psi \rangle && \text{given } \langle x_0 | \hat{X} | \psi \rangle \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx_0 \left(e^{-ip_0x_0/\hbar} x_0 \right) \langle x_0 | \psi \rangle && \text{given } \langle x_0 | \hat{X} | \psi \rangle \\ &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx_0 \left(i\hbar \frac{\partial}{\partial p_0} e^{-ip_0x_0/\hbar} \right) \langle x_0 | \psi \rangle \\ &= \int_{-\infty}^{\infty} dx_0 \left(i\hbar \frac{\partial}{\partial p_0} \right) \langle p_0 | x_0 \rangle \langle x_0 | \psi \rangle && \text{Go back now} \\ &= \left(i\hbar \frac{\partial}{\partial p_0} \right) \langle p_0 | \psi \rangle && \text{Integrate over } x_0 \blacksquare \end{aligned}$$

- Here is a table to collect the results:

	Position Rep.	Momentum Rep.
Position Op.	$\hat{X}f(x) = xf(x)$	$\hat{X}f(p_x) = i\hbar \frac{\partial}{\partial p_x} f(p_x)$
Momentum Op.	$\hat{P}_x f(x) = -i\hbar \frac{d}{dx} f(x)$	$\hat{P}_x f(p_x) = p_x f(p_x)$

2 Postulates of Quantum Mechanics

2.1 Statement of the postulates

Definition: Quantum Postulate 1

At a fixed time t_0 , the state of a physical system is defined by specifying a ket $|\psi(t_0)\rangle$ belonging to the state space \mathcal{E} .

[Corresponds to Postulate 1 in Atkins and Friedman]

Definition: Quantum Postulate 2

Every measurable quantity \mathcal{A} is described by a Hermitian operator $\hat{\mathcal{A}}$ acting in \mathcal{E} ; this operator is an observable, and can be expressed as a function of operators \hat{R} and \hat{P} .

[Corresponds to Postulate 2 in Atkins and Friedman]

- Example: Hamiltonian operator

- Consider the classical Hamiltonian for one particle (sum of kinetic and potential energies)

$$\mathcal{H}(r, p) = \frac{p^2}{2m} + V(r)$$

- obtain quantum Hamiltonian operator by replacing dynamic variables with operators:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{R})$$

- Position representation:

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

Definition: Quantum Postulate 3

The only possible result of the measurement of a physical quantity \mathcal{A} is one of the eigenvalues of the corresponding observable $\hat{\mathcal{A}}$.

[Corresponds to Postulate 3 and 3' in Atkins and Friedman]

- Comments:

- Since Observables are Hermitian operators, measurements only give real values
 - If the spectrum of an operator is discrete, this system must be “quantized”

Definition: Quantum Postulate 4

(Case of a non-degenerate discrete spectrum)

When the physical quantity \hat{A} is measured on a system in a normalized state $|\psi\rangle$, the probability of observing the eigenvalue a_n of the corresponding operator \hat{A} is:

$$\begin{aligned}\mathcal{P}(a_n) &= |\langle u_n | \psi \rangle|^2 \\ &= |c_n|^2\end{aligned}$$

where, $|u_n\rangle$ is the eigenvector of \hat{A} corresponding to eigenvalue a_n .

[Corresponds to Postulate 4 in Atkins and Friedman]

● Comments:

- Assume, system is in state $|\psi\rangle$, and an operator has eigenvectors: $\hat{A}|\lambda_n\rangle = \lambda_n|\lambda_n\rangle$.
Expectation value is the average value obtained after making many measurements:

$$\begin{aligned}\langle \hat{A} \rangle &= \langle \psi | \hat{A} | \psi \rangle && \text{definition} \\ &= \sum_{nm} \langle \psi | |\lambda_m\rangle \langle \lambda_m | \hat{A} | \lambda_n \rangle \langle \lambda_n | \psi \rangle && \text{RI} \\ &= \sum_{nm} \lambda_n \langle \psi | \lambda_m \rangle \langle \lambda_m | \lambda_n \rangle \langle \lambda_n | \psi \rangle && \text{eigenvalue} \\ &= \sum_n \lambda_n \langle \psi | \lambda_n \rangle \langle \lambda_n | \psi \rangle && \text{orthogonality of } m, n \\ &= \sum_n \lambda_n |c_n|^2 && \text{weighted average}\end{aligned}$$

- Each individual measurement returns one eigenvalue, weighted by the squared modulus of the coefficient, as stated by the postulate.
- If $|\psi\rangle$ happens to be an eigenstate of \hat{A} , then it will always give the corresponding eigenvalue
- Note:

$$|c_n|^2 = c_n^* c_n = \langle \psi | u_n \rangle \langle u_n | \psi \rangle \quad (125)$$

$$= \langle \psi | \hat{P}_n | \psi \rangle \quad (126)$$

Definition: Quantum Postulate 5

If the measurement of the physical quantity \hat{A} on the system in state $|\psi\rangle$ gives the result a_n , the state of the system immediately after the measurement is the normalized projection, of $|\psi\rangle$ onto the eigensubspace associated with a_n :

$$|\psi\rangle \xrightarrow{a_n} \frac{\hat{P}_n |\psi\rangle}{\sqrt{\langle \psi | \hat{P}_n | \psi \rangle}},$$

This is referred to as wavefunction collapse

[Corresponds to Postulate 3 and 3' in Atkins and Friedman]

- Comments:

- Considering two sequential measurements of \hat{A} justifies this
- What does this say about commuting observables, $[\hat{A}, \hat{B}] = 0$?
 - * What if we measure \hat{A} , then immediately measure \hat{B} ? (assume non-degenerate eigenvalues)
- Uncertainty

Definition: Quantum Postulate 6

The time evolution of the state vector $|\psi(t)\rangle$ is governed by the Schrödinger equation:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle,$$

where $\hat{H}(t)$ is the Hamiltonian operator, or the Hermitian operator associated with the total energy of the system.

[Corresponds to Postulate 5 in Atkins and Friedman]

Start of Lecture 6

2.2 Separation of variables: TDSE → TISE

- For time-independent Potential $V(x) \neq f(t)$:

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] |\psi(t)\rangle \quad \text{TDSE}$$

- Position and Time are separable, so we assume the following solution form:

$$|\psi(t)\rangle = \Psi(x, t) = \psi(x)\theta(t) \quad \text{Position representation}$$

- Substitute into TDSE

$$\begin{aligned} i\hbar \frac{d}{dt} \psi(x)\theta(t) &= \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x)\theta(t) \\ \psi(x)i\hbar \frac{d}{dt} \theta(t) &= \theta(t) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) \quad \text{Rearrange} \\ \frac{1}{\theta(t)} i\hbar \frac{d}{dt} \theta(t) &= \frac{1}{\psi(x)} \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) \quad \text{divide by } \psi(x)\theta(t) \end{aligned}$$

- Since LHS depends only on t , and RHS depends only on x , the equality means that both must equal a constant:

$$\begin{aligned} E &= \frac{1}{\theta(t)} i\hbar \frac{d}{dt} \theta(t) && \text{constant } E \\ &= \frac{1}{\psi(x)} \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) \end{aligned}$$

- Yields two equations:

$$\begin{aligned} E\theta(t) &= i\hbar \frac{d}{dt} \theta(t) && \text{time equation} \\ E\psi(x) &= \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) && \text{space equation} \\ E\psi(x) &= \hat{H}\psi(x) && \text{TISE} \end{aligned}$$

- Time equation is easy:

$$\theta(t) = e^{-\frac{i}{\hbar} Et} \quad \text{time solution}$$

- Thus:

$$\Psi(x, t) = \psi(x) e^{-\frac{i}{\hbar} Et}$$

- Even for time-independent Hamiltonian, wavefunction evolves in time??
- Yes, but the wavefunction is not an observable. What about probability density?

$$\begin{aligned} \Psi(x, t)^* \Psi(x, t) &= \psi(x)^* e^{\frac{i}{\hbar} Et} \psi(x) e^{-\frac{i}{\hbar} Et} \\ &= \psi(x)^* \psi(x) \\ &\neq f(t) && \psi(x) \text{ is a stationary state} \end{aligned}$$

2.3 Uncertainty Principle

- Assume for two observables, \hat{A} and \hat{B} ,

$$[\hat{A}, \hat{B}] = i\hat{C}$$

- Consider a state $|\phi\rangle = (\hat{A} + i\lambda\hat{B}) |\psi\rangle$
- For any λ the squared norm must be non-negative:

$$\langle \phi | \phi \rangle \geq 0$$

$$\begin{aligned} \langle \phi | \phi \rangle &= \langle \psi | (\hat{A} - i\lambda\hat{B}) (\hat{A} + i\lambda\hat{B}) | \psi \rangle && \text{by definition} \\ &= \langle \hat{A}^2 \rangle + i\lambda \langle [\hat{A}, \hat{B}] \rangle + \lambda^2 \langle \hat{B}^2 \rangle && \text{expand terms} \\ &= \langle \hat{A}^2 \rangle - \lambda \langle \hat{C} \rangle + \lambda^2 \langle \hat{B}^2 \rangle \end{aligned}$$

$$\langle \phi | \phi \rangle = \langle \hat{B}^2 \rangle \left(\lambda - \frac{\langle \hat{C} \rangle}{2 \langle \hat{B}^2 \rangle} \right)^2 + \langle \hat{A}^2 \rangle - \frac{\langle \hat{C} \rangle^2}{4 \langle \hat{B}^2 \rangle} \geq 0 \quad \text{completing the square}$$

Remember how to complete the square?

$$ax^2 + bx + c = a \left(x + \frac{b}{2a} \right)^2 + c - \frac{b^2}{4a}$$

- For this to always be true for any value of λ , even when it makes the red term zero:

$$\begin{aligned} \langle \hat{A}^2 \rangle - \frac{\langle \hat{C} \rangle^2}{4\langle \hat{B}^2 \rangle} &\geq 0 && \text{since } \lambda \text{ is arbitrary} \\ \langle \hat{A}^2 \rangle \langle \hat{B}^2 \rangle &\geq \frac{\langle \hat{C} \rangle^2}{4} && \text{rearranging} \end{aligned}$$

- This is true for any two Hermitian operators
- Consider the following “spread” operator:

$$\begin{aligned} \delta \hat{A} &= \hat{A} - \langle \hat{A} \rangle && \text{commutator} \\ [\delta \hat{A}, \delta \hat{B}] &= [\hat{A}, \hat{B}] - [\hat{A}, \langle \hat{B} \rangle] - [\langle \hat{A} \rangle, \hat{B}] + [\langle \hat{A} \rangle, \langle \hat{B} \rangle] && \text{Expectation value = scalar} \\ &= [\hat{A}, \hat{B}] && \text{definition above} \\ &= i\hat{C} && \text{also Hermitian} \\ \delta \hat{A} &= \delta \hat{A}^\dagger \end{aligned}$$

- Thus, this also must hold:

$$\begin{aligned} \langle \delta \hat{A}^2 \rangle \langle \delta \hat{B}^2 \rangle &\geq \frac{\langle \hat{C} \rangle^2}{4} && \text{rearranging} \\ \langle \delta \hat{A}^2 \rangle \langle \delta \hat{B}^2 \rangle &= \langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle \langle (\hat{B} - \langle \hat{B} \rangle)^2 \rangle && \text{expanding} \\ &= (\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2) (\langle \hat{B}^2 \rangle - \langle \hat{B} \rangle^2) && \text{expanding} \end{aligned}$$

- Thus, taking square root we get the famous Heisenberg uncertainty principle :

$$\begin{aligned} \Delta \hat{A} \Delta \hat{B} &\geq \frac{|\langle \hat{C} \rangle|}{2} && \text{square root} \\ &\text{or} \\ \Delta \hat{A} \Delta \hat{B} &\geq \frac{|\langle [\hat{A}, \hat{B}] \rangle|}{2} \end{aligned}$$

- Where we have introduced the root mean square deviation or RMSD :

$$\Delta \hat{A} = \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}$$

Example: position and momentum

$$\Delta \hat{x} \Delta \hat{p}_x \geq \frac{\hbar}{2}$$

2.4 Time-evolution of expectation values

- Take derivative

$$\begin{aligned} \frac{\partial}{\partial t} \langle \hat{A} \rangle &= \frac{\partial}{\partial t} \langle \psi | \hat{A} | \psi \rangle && \text{definition} \\ &= \left\langle \frac{\partial}{\partial t} \psi \middle| \hat{A} \middle| \psi \right\rangle + \langle \psi | \frac{\partial}{\partial t} \hat{A} | \psi \rangle + \left\langle \psi \middle| \hat{A} \middle| \frac{\partial}{\partial t} \psi \right\rangle \end{aligned}$$

- remember TDSE

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} |\psi\rangle &= \hat{H} |\psi\rangle \\ -i\hbar \frac{\partial}{\partial t} \langle \psi | &= \langle \psi | \hat{H} \end{aligned}$$

- Substitute

$$\begin{aligned} \frac{\partial}{\partial t} \langle \hat{A} \rangle &= \frac{-1}{i\hbar} \langle \psi | \hat{H} \hat{A} | \psi \rangle + \langle \psi | \frac{\partial}{\partial t} \hat{A} | \psi \rangle + \frac{1}{i\hbar} \langle \psi | \hat{A} \hat{H} | \psi \rangle \\ &= \frac{i}{\hbar} \langle \psi | [\hat{H}, \hat{A}] | \psi \rangle + \langle \psi | \frac{\partial}{\partial t} \hat{A} | \psi \rangle \end{aligned}$$

- If $\hat{A} \neq f(t)$ then,

$$\frac{\partial}{\partial t} \langle \hat{A} \rangle = \frac{i}{\hbar} \langle \psi | [\hat{H}, \hat{A}] | \psi \rangle$$

- Anything that commutes with the Hamiltonian is a constant of motion!

Definition: **constant of motion**

is a quantity that is conserved throughout the motion, imposing in effect a constraint on the motion

- What if $\hat{A} = \hat{H} \neq f(t)$?

$$\begin{aligned} \frac{\partial}{\partial t} \langle \hat{H} \rangle &= \frac{i}{\hbar} \langle \psi | [\hat{H}, \hat{H}] | \psi \rangle \\ &= 0 \end{aligned}$$

- Energy is clearly a constant of motion!
- Is momentum a constant of motion? Yes, for a free particle (zero potential)

Start of Lecture 7

3 Linear motion

3.1 Free particle wavefunctions

- Consider simplest case: constant potential ($V(x) = 0$) Hamiltonian for single particle in 1D

$$\hat{H} = \frac{\hat{p}_x^2}{2m} \xrightarrow[\text{representation}]{\text{position}} -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

such that we seek solutions of the TDSE:

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} |\psi\rangle$$

- Since \hat{H} is independent of time,

$$\begin{aligned} |\psi(t)\rangle &= |\psi\rangle \phi(t) && \text{Sep. of vars} \\ &= |\psi\rangle e^{-iEt/\hbar} \end{aligned}$$

- What is $|\psi\rangle$? Eigenvalue of $\frac{d^2}{dx^2}$, thus $Ae^{\pm ikx}$ is a solution

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} |\psi\rangle &= \frac{\hbar^2}{2m} k^2 A e^{\pm ikx} \\ &= \frac{k^2 \hbar^2}{2m} |\psi\rangle \\ &= E |\psi\rangle \end{aligned}$$

thus,

$$E = \frac{k^2 \hbar^2}{2m}$$

- what is k ? Consider momentum operator in position representation

$$\begin{aligned} \hat{p}_x |\psi\rangle &= -i\hbar \frac{\partial}{\partial x} A e^{ikx} \\ &= k\hbar A e^{ikx} \\ &= k\hbar |\psi\rangle \end{aligned}$$

$$\text{Thus, } p_x = \pm k\hbar$$

- $|\psi\rangle$ is therefore an eigenvalue of both \hat{H} and \hat{p}_x , with $\pm k\hbar$ eigenvalue being equal to the momentum in x-direction

$$\begin{aligned} |\psi\rangle &= Ae^{ikx} \\ |\psi\rangle &= Ae^{-ikx} \end{aligned}$$

Forward momentum state

Backward momentum state

- Total wavefunction: substitute for E

$$\begin{aligned} |\psi(t)\rangle &= |\psi\rangle e^{-i\frac{\hbar k^2}{2m}t} \\ &= |\psi\rangle e^{-i\omega t} \\ &= Ae^{ikx}e^{-i\omega t} \\ &= Ae^{i(kx-\omega t)} \end{aligned}$$

where, $\omega = \frac{\hbar k^2}{2m}$

Definition: plane wave

A plane wave has the following form:

$$|\psi(t)\rangle = Ae^{i(kx-\omega t)}$$

Definition: dispersion relation

A free particle has the following dispersion relation, which relates the angular frequency $\omega = 2\pi f$, to the wavenumber k :

$$\omega(k) = \frac{\hbar k^2}{2m}$$

- Unlike \hat{p}_x , the total energy operator \hat{H} also has eigenvectors which are linear combinations of left and right states
 - Does this make sense? Think of the properties of degenerate eigenvalues of Hermitian operators.
 - therefore, the energy eigenstates have a more general form of being linear combinations of left and right states
 - if $|\psi\rangle = Ae^{ikx} + Be^{-ikx}$,

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} |\psi\rangle &= -\frac{\hbar^2}{2m} \left(-k^2 Ae^{ikx} + -k^2 Be^{-ikx} \right) \\ &= \frac{k^2 \hbar^2}{2m} \left(Ae^{ikx} + Be^{-ikx} \right) \\ &= E |\psi\rangle \end{aligned}$$

3.1.1 Wavepackets

- A single plane wave is not square-integrable, and thus cannot be a description of a physical state

$$\int_{-\infty}^{\infty} dx \left(A^* A e^{-i(kx - \omega t)} e^{i(kx - \omega t)} \right) = |A|^2 x \Big|_{-\infty}^{\infty} = \infty$$

- To get a good state, we use the fact that since the Schrödinger equation is a linear differential equation, a linear superposition of solutions is also a solution.

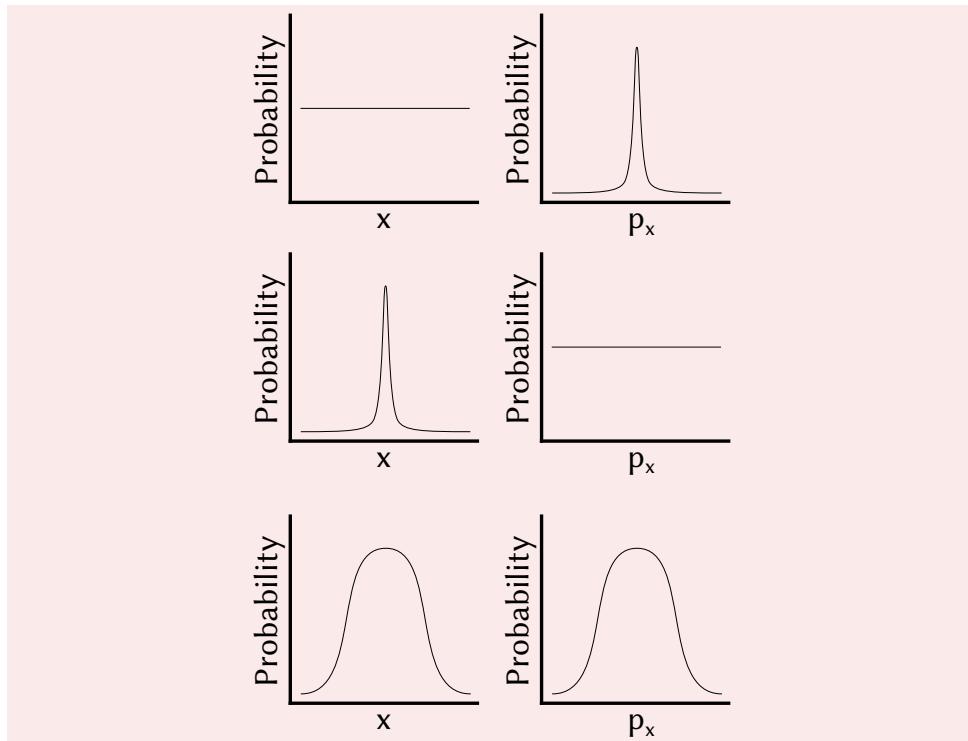
$$|\psi(t)\rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk g(k) e^{i(kx - \omega t)} \quad \text{linear combination}$$

3.1.2 Wavepackets at a given instant

- If we consider the wavepacket at only a given instant $t = t_0$:

$$|\psi\rangle = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk g(k) e^{ikx} \quad \text{at } t_0 = 0$$

we see that $g(k)$ is the Fourier transform of wavefunction, and it is called the **shape function**.

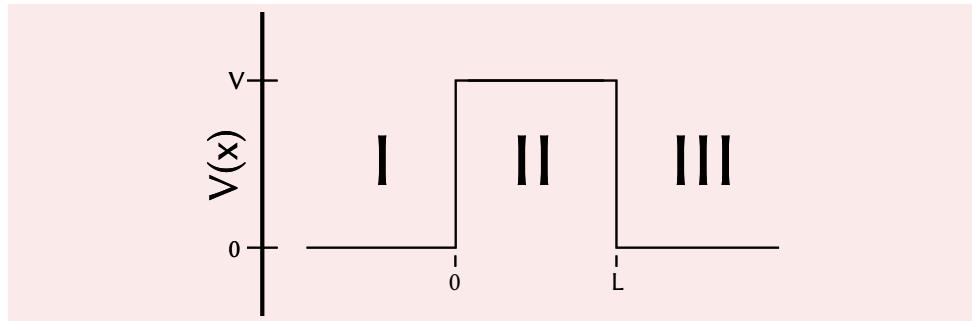


- wavepackets spread out in time

- At $t = 0$ we have a localized wavefunction about $x = x_0$, with momentum localized about $k = k_0$

- At $t = \Delta t$, the bulk of the wavepacket has translated according to momentum k , but some probability of smaller and larger momentum exists
- Thus some of the wavepacket moves slowly, some moves faster, resulting in a spreading out of the wavepacket
- consider a perfectly localized in space function as an example

3.2 Scattering across a finite barrier



- Schrödinger equations:

- Zone 1:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x)$$

- Zone 2:

$$\begin{aligned} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V \right) \psi(x) &= E\psi(x) \\ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) &= (E - V) \psi(x) \end{aligned}$$

- Zone 3:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x)$$

- Solutions:

$$\psi_I(x) = A e^{ikx} + B e^{-ikx} \quad \text{with } k = \frac{\sqrt{2mE}}{\hbar}$$

$$\psi_{II}(x) = A' e^{ik'x} + B' e^{-ik'x} \quad \text{with } k' = \frac{\sqrt{2m(E-V)}}{\hbar}$$

$$\psi_{III}(x) = A'' e^{ikx} + B'' e^{-ikx}$$

Case 1: $E < V$

- $k' = \sqrt{2m(E - V)}/\hbar = i\kappa$
- At $x = 0$

$$\begin{aligned}\psi_I(0) &= \psi_{II}(0) && \text{continuity} \\ \frac{d}{dx}\psi_I(0) &= \frac{d}{dx}\psi_{II}(0) && \text{smooth}\end{aligned}$$

$$\begin{aligned}Ae^{ikx} + Be^{-ikx} &= A'e^{-\kappa x} + B'e^{\kappa x} \Big|_{x=0} \\ ikAe^{ikx} - ikBe^{-ikx} &= -\kappa A'e^{-\kappa x} + \kappa B'e^{\kappa x} \Big|_{x=0}\end{aligned}$$

$$\begin{aligned}A + B &= A' + B' \\ ikA - ikB &= -\kappa A' + \kappa B'\end{aligned}$$

- At $x = L$

$$\begin{aligned}\psi_{II}(L) &= \psi_{III}(L) && \text{continuity} \\ \frac{d}{dx}\psi_{II}(L) &= \frac{d}{dx}\psi_{III}(L) && \text{smooth}\end{aligned}$$

$$\begin{aligned}A'e^{-\kappa L} + B'e^{\kappa L} &= A''e^{ikL} + B''e^{-ikL} \\ -\kappa A'e^{-\kappa L} + \kappa B'e^{\kappa L} &= ikA''e^{ikL} - ikB''e^{-ikL}\end{aligned}$$

- We've got 6 unknowns, but only 4 equations:
 - Normalization
 - Initial Condition, particle starts at $-\infty$ with positive momentum: $B'' = 0$



- Important coefficients:
 - B = Reflection
 - A'' = Transmission
- How “much” of the wavefunction is being reflected?

- Reflection is the ratio of reflected flux density to incident flux density

$$1 = \frac{J_{out}}{J_{in}} = \frac{J_{\leftarrow} + J_{\rightarrow}}{J_{in}} = R + T$$

Definition: flux density

In one dimension, the flux density is given as:

$$\begin{aligned} J_x &= \frac{1}{2m} (\psi^* \hat{p} \psi + \psi \hat{p}^* \psi^*) \\ &= \frac{-i\hbar}{2m} \psi^*(x) \frac{\partial}{\partial x} \psi(x) + C.C. \end{aligned}$$

- Calculate J_{\leftarrow}

$$\begin{aligned} J_{\leftarrow} &= \frac{-i\hbar}{2m} (Be^{-ikx})^* \frac{d}{dx} (Be^{-ikx}) + C.C. && \text{definition} \\ &= \frac{-i\hbar}{2m} (B^* e^{ikx}) (Be^{-ikx}) (-ik) + C.C. \\ &= \frac{-k\hbar}{2m} |B|^2 + C.C. \\ &= \frac{-k\hbar}{m} |B|^2 \end{aligned}$$

- Calculate J_{in}

$$\begin{aligned} J_{in} &= \frac{-i\hbar}{2m} (Ae^{ikx})^* \frac{d}{dx} (Ae^{ikx}) + C.C. && \text{definition} \\ &= \frac{k\hbar}{m} |A|^2 \end{aligned}$$

- thus,

$$\begin{aligned} R &= -\frac{|B|^2}{|A|^2} \\ T &= 1 - R \end{aligned}$$

- Solving for R and T in terms of the wavefunction coefficients requires only basic (but tedious!) algebra - we will skip this and just post the results

$$T = \frac{1}{1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16(E/V)(1-E/V)}} \quad \text{When } E < V$$

- Likewise, we can repeat the procedure to find the case when $E > V$

$$T = \frac{1}{1 + \frac{\sin^2(k'L)}{4(E/V)(E/V-1)}} \quad \text{When } E > V$$

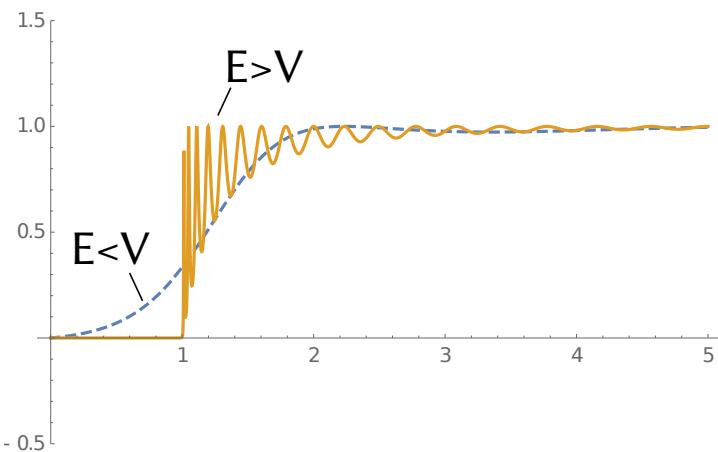
- and

$$T = \frac{1}{1 + \frac{L^2 m V}{2 \hbar^2}}$$

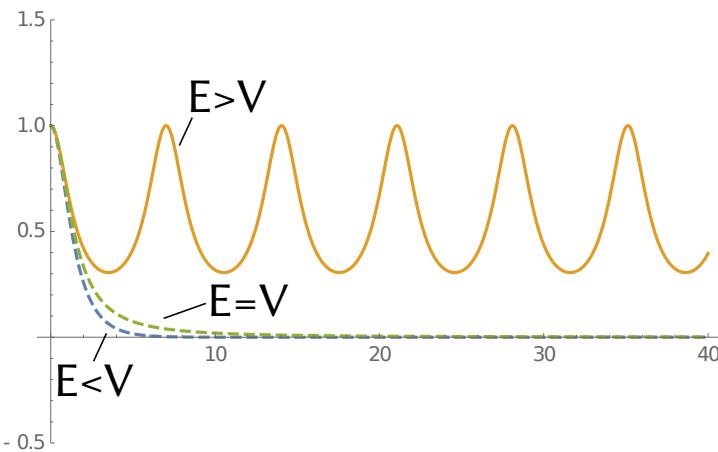
When $E = V$

- Let's plot these transmission coefficients

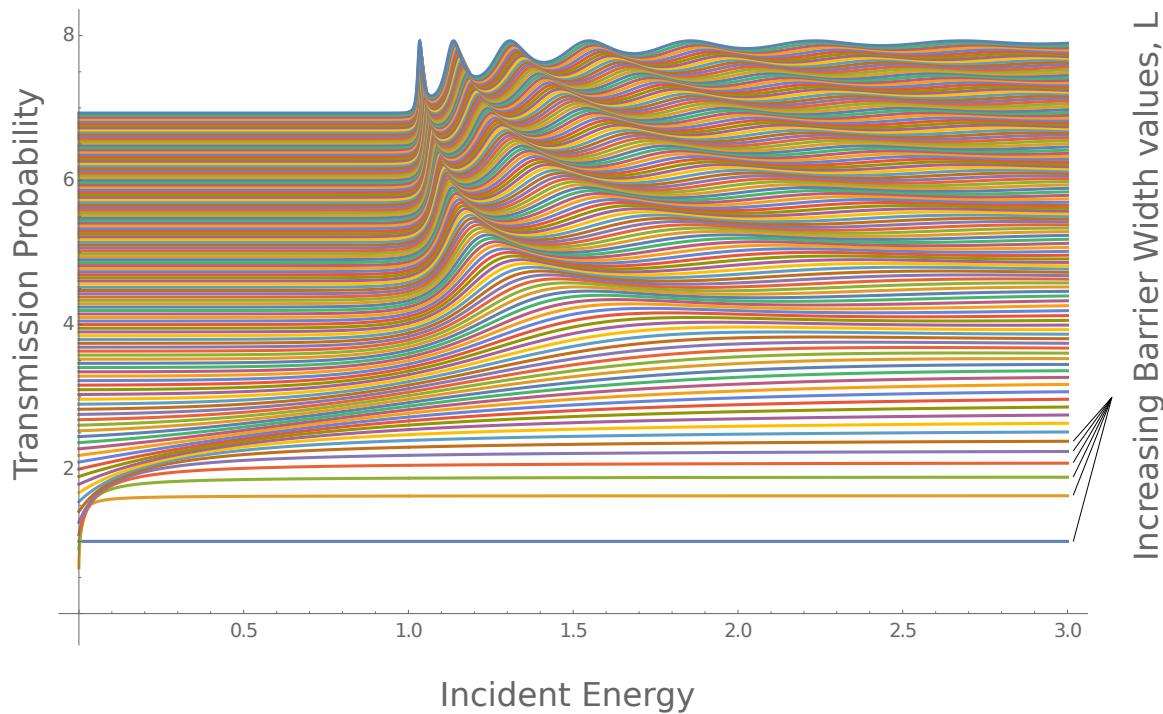
- Function of incident energy (remember, T_1 (T_2) is only defined when $E < V$ ($E > V$))



- Function of barrier width



- Function of both



- When does $T \rightarrow 1$ as a function of L ? This happens when,

$$\begin{aligned} k'L &= n\pi \\ &= \frac{\sqrt{2m(E - V)}L}{\hbar} \end{aligned} \quad \text{from T where } E > V$$

so,

$$L = \frac{n\pi\hbar}{\sqrt{2m(E - V)}}$$

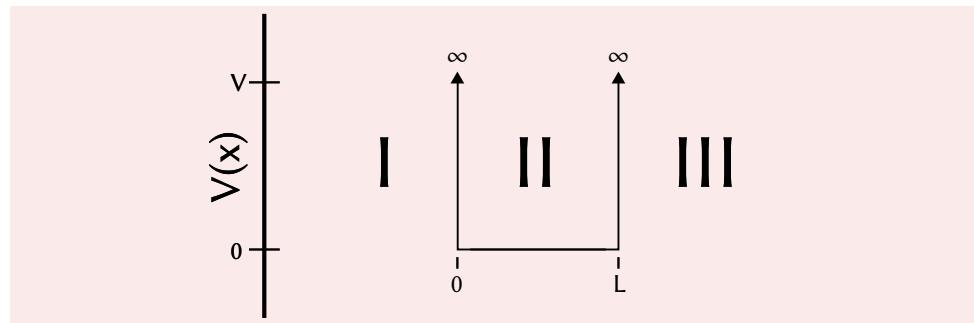
- As $L \rightarrow \infty$, $T_{E \leq V} \rightarrow 0$, $T_{E > V} \rightarrow 1$
- As $L \rightarrow 0$, $T \rightarrow 1$
- As $V \rightarrow \infty$, $T \rightarrow 0$
- As $m \rightarrow \infty$, $T_{E \leq V} \rightarrow 0$, $T_{E > V} \rightarrow 1$

Start of Lecture 8

3.3 Particle in a box

- So we have observed only free-particles, no attractive potentials.

- Consider now the following potential



- Trial wavefunction

$$\psi(x) = A e^{ikx} + B e^{-ikx}$$

- Boundary conditions:

$$\begin{aligned}\psi(0) &= \psi(L) = 0 \\ A + B &= 0 \\ A e^{ikL} + B e^{-ikL} &= 0\end{aligned}\Rightarrow A = -B$$

- Thus,

$$\begin{aligned}A \left(e^{ikL} - e^{-ikL} \right) &= 0 \\ 2iA \sin(kL) &= 0 \quad \text{Euler relation} \\ \text{Thus,} \\ kL &= n\pi \quad \text{for } n = 0, 1, 2, \dots\end{aligned}$$

Remember Euler relation :

$$e^{ix} = \cos(x) + i \sin(x)$$

Leading to,

$$\begin{aligned}\frac{e^{ix} + e^{-ix}}{2} &= \cos(x) \\ \frac{e^{ix} - e^{-ix}}{2i} &= \sin(x)\end{aligned}$$

- We get energy quantization!

$$kL = L \frac{\sqrt{2mE}}{\hbar} = n\pi \quad \text{From above}$$

$$E = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad \text{or } \frac{n^2 \hbar^2}{8mL^2}$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

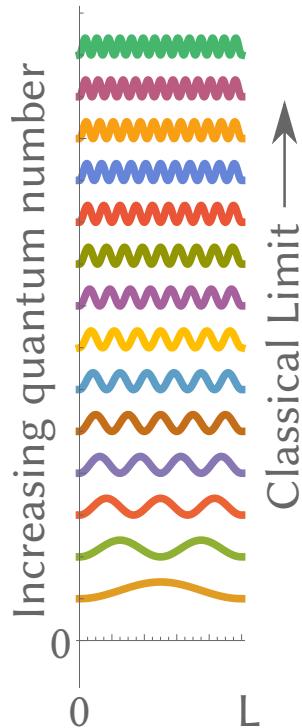
- What about $n = 0$?

$$\psi(x) = 0 \quad \text{no particle!}$$

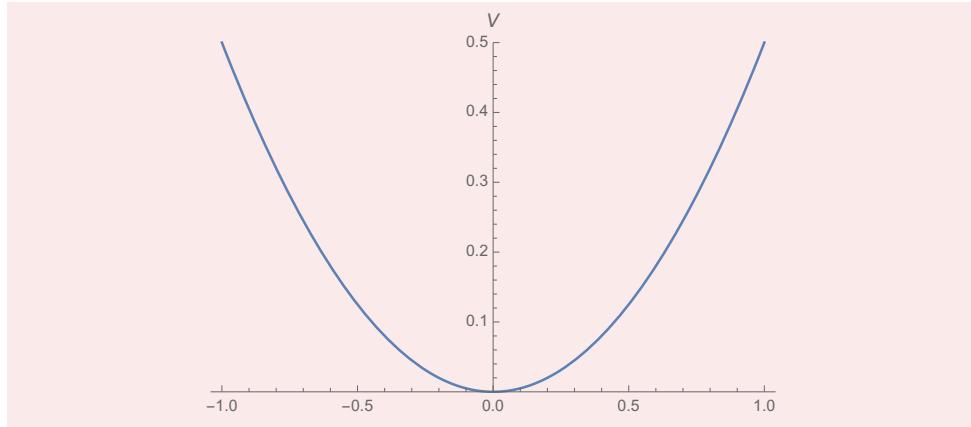
- For a particle to exist, $n = 1, 2, 3, \dots$
- Thus the minimum energy is

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2} \quad \text{zero-point energy}$$

- distribution inside of box



3.4 Harmonic Oscillator



- Schrödinger equation

$$\left(\frac{\hat{P}_x^2}{2m} + \frac{1}{2}m\omega^2 \hat{X}^2 \right) |\psi\rangle = E |\psi\rangle \quad \text{where } \omega \text{ is angular frequency}$$

- To simplify things, let's use dimensionless quantities

$$\begin{aligned}\hat{H}' &= \frac{\hat{H}}{\hbar\omega} \\ &= \frac{1}{2} \left(\frac{1}{m\hbar\omega} \hat{P}^2 + \frac{m\omega}{\hbar} \hat{X}^2 \right) \\ &= \frac{1}{2} (\hat{P}'^2 + \hat{X}'^2) \\ E' &= \frac{E}{\hbar\omega}\end{aligned}$$

– where we define the dimensionless operators:

$$\begin{aligned}\hat{X}' &= \sqrt{\frac{m\omega}{\hbar}} \hat{X} \\ \hat{P}' &= \sqrt{\frac{1}{m\hbar\omega}} \hat{P}\end{aligned}$$

– How does the affect the commutator?

$$\begin{aligned}[\hat{X}', \hat{P}'] &= \hat{X}' \hat{P}' - \hat{P}' \hat{X}' \\ &= \sqrt{\frac{m\omega}{\hbar}} \hat{X} \sqrt{\frac{1}{m\hbar\omega}} \hat{P} - \sqrt{\frac{1}{m\hbar\omega}} \hat{P} \sqrt{\frac{m\omega}{\hbar}} \hat{X} \\ &= \frac{1}{\hbar} [\hat{X}, \hat{P}] \\ [\hat{X}', \hat{P}'] &= i\end{aligned}$$

- Let's try solving the SE by factorization. If \hat{P}' and \hat{X}' were just numbers, we could easily factor this into a binomial.

$$a^2 + b^2 = (a - ib)(a + ib)$$

- But this doesn't work for operators,

$$\begin{aligned} (\hat{X}' - i\hat{P}')(\hat{X}' + i\hat{P}') &= \hat{X}'^2 + \hat{P}'^2 + i[\hat{X}', \hat{P}'] \\ &= \hat{X}'^2 + \hat{P}'^2 - 1 \end{aligned}$$

- But it does give us something useful:

$$\hat{H}' = \frac{1}{2} [(\hat{X}' - i\hat{P}')(\hat{X}' + i\hat{P}') + 1]$$

- Let's define the following non-Hermitian operator:

$$\begin{aligned} \hat{a} &= \frac{1}{\sqrt{2}} (\hat{X}' + i\hat{P}') && \text{annihilation operator} \\ \hat{a} &= \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m\omega}{\hbar}} \hat{X} + i\sqrt{\frac{1}{m\hbar\omega}} \hat{P} \right) && \text{in original units} \end{aligned}$$

such that

$$\hat{H}' = \hat{a}^\dagger \hat{a} + \frac{1}{2}$$

and

$$\hat{H}' |\lambda\rangle = \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right) |\lambda\rangle = E'_\lambda |\lambda\rangle$$

- This operator has the following commutator:

$$\begin{aligned} [\hat{a}, \hat{a}^\dagger] &= \frac{1}{2} [\hat{X}' + i\hat{P}', \hat{X}' - i\hat{P}'] \\ &= \frac{1}{2} ([\hat{X}', \hat{X}] - i[\hat{X}', \hat{P}'] + i[\hat{P}', \hat{X}'] + [\hat{P}', \hat{P}']) \\ &= -i[\hat{X}', \hat{P}'] \\ &= 1 \end{aligned}$$

- Consider the operator $\hat{a}^\dagger \hat{a} = \hat{N}$,

- \hat{N} commutes with the Hamiltonian

$$\begin{aligned} \hat{a}^\dagger \hat{a} |\lambda\rangle &= \left(E'_\lambda - \frac{1}{2} \right) |\lambda\rangle \\ &= \lambda |\lambda\rangle \\ \langle \lambda | \hat{a}^\dagger \hat{a} | \lambda \rangle &= \left(E'_\lambda - \frac{1}{2} \right) && \text{Mult. by } \langle \lambda | \\ &= (\hat{a} | \lambda \rangle)^\dagger (\hat{a} | \lambda \rangle) \geq 0 && \text{norm squared} \end{aligned}$$

- Thus we see that the energy has a minimum value

$$\begin{aligned} E' &\geq \frac{1}{2} && \text{norm squared} \\ E &\geq \frac{\hbar\omega}{2} && \text{original units} \end{aligned}$$

- This minimum value is the zero-point energy

Start of Lecture 9

- What is the effect of the operator \hat{a} ?

$$\begin{aligned} \hat{a}\hat{a}^\dagger\hat{a}|\lambda\rangle &= \lambda\hat{a}|\lambda\rangle && \text{left mult. by } \hat{a} \\ (\hat{a}^\dagger\hat{a} + 1)\hat{a}|\lambda\rangle &= \lambda\hat{a}|\lambda\rangle && \text{use commutator} \\ (\hat{a}^\dagger\hat{a})\hat{a}|\lambda\rangle &= (\lambda - 1)\hat{a}|\lambda\rangle && \text{Eigenvalue shifted down} \end{aligned}$$

- thus

$$\hat{a}|\lambda\rangle \propto |\lambda - 1\rangle$$

- Can we continue to lower the energy indefinitely by application of \hat{a} ? No. Since,

$$\langle\lambda|\hat{a}^\dagger\hat{a}|\lambda\rangle \geq 0$$

The only way for the equality to hold, is if

$$\hat{a}|0\rangle = 0 \quad \hat{a} \text{ stops at ground state}$$

- What is the effect of the operator \hat{a}^\dagger ?

$$\begin{aligned} \hat{a}^\dagger\hat{a}^\dagger\hat{a}|\lambda\rangle &= \lambda\hat{a}^\dagger|\lambda\rangle && \text{left mult. by } \hat{a}^\dagger \\ \hat{a}^\dagger(\hat{a}\hat{a}^\dagger - 1)|\lambda\rangle &= \lambda\hat{a}^\dagger|\lambda\rangle && \text{use commutator} \\ (\hat{a}^\dagger\hat{a})\hat{a}^\dagger|\lambda\rangle &= (\lambda + 1)\hat{a}^\dagger|\lambda\rangle && \text{Eigenvalue shifted up} \end{aligned}$$

thus

$$\hat{a}^\dagger|\lambda\rangle \propto |\lambda + 1\rangle$$

- So \hat{a} is a lowering operator, (also called annihilation operator) and \hat{a}^\dagger is a raising operator (A.K.A creation operator)

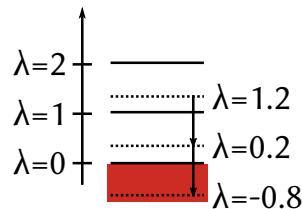
- Proportionality constants

$$\begin{aligned}
 \hat{a} |\lambda\rangle &= k_{\lambda-1} |\lambda-1\rangle \propto |\lambda-1\rangle \\
 \langle \lambda | \hat{a}^\dagger \hat{a} | \lambda \rangle &= \lambda \\
 &= |k_{\lambda-1}|^2 \\
 k_{\lambda-1} &= \sqrt{\lambda} \quad \lambda \text{ is } \geq 0 \\
 \hat{a} |\lambda\rangle &= \sqrt{\lambda} |\lambda-1\rangle
 \end{aligned}$$

$$\begin{aligned}
 \hat{a}^\dagger |\lambda\rangle &= k_{\lambda+1} |\lambda+1\rangle \propto |\lambda+1\rangle \\
 \langle \lambda | \hat{a} \hat{a}^\dagger | \lambda \rangle &= \langle \lambda | 1 + \hat{a}^\dagger \hat{a} | \lambda \rangle \\
 &= \lambda + 1 \\
 &= |k_{\lambda+1}|^2 \\
 k_{\lambda+1} &= \sqrt{\lambda+1} \\
 \hat{a}^\dagger |\lambda\rangle &= \sqrt{\lambda+1} |\lambda+1\rangle
 \end{aligned}$$

- What values are permitted for λ ?

- We know $\langle \lambda | \hat{a}^\dagger \hat{a} | \lambda \rangle = \lambda \geq 0$
- We know $\hat{a} |\lambda\rangle = \sqrt{\lambda} |\lambda-1\rangle$



- Only non-negative integers of λ allow these conditions to be true, thus λ is quantized!

Harmonic Oscillator energies

$$\begin{aligned}
 E'_\lambda &= \left(\lambda + \frac{1}{2} \right) \\
 E_\lambda &= \hbar\omega \left(\lambda + \frac{1}{2} \right) \quad \forall \lambda \in \{0, 1, 2, \dots\}
 \end{aligned}$$

- All states equally spaced

- What do the eigenstates look like?

- Use $\hat{a} |0\rangle = 0$
- Let's use position representation

$$\begin{aligned}\hat{a} |0\rangle &\rightarrow \frac{1}{\sqrt{2}} (\hat{X}' + i\hat{P}') \phi_0(x) = 0 && \text{where, } \phi_0(x) = \langle x|0\rangle \\ &= \left(\sqrt{\frac{m\omega}{\hbar}}x + \sqrt{\frac{1}{m\hbar\omega}}\hbar\frac{d}{dx} \right) \phi_0(x) \\ &= \left(x + \frac{\hbar}{m\omega}\frac{d}{dx} \right) \phi_0(x)\end{aligned}$$

- Solve the following simple differential equation

$$\begin{aligned}-x\phi_0(x) &= \frac{\hbar}{m\omega}\frac{d}{dx}\phi_0(x) && \text{multiply by } \frac{dx}{\phi_0(x)} \\ -xdx &= \frac{\hbar}{m\omega}\frac{1}{\phi_0(x)}d\phi_0(x) && \text{integrate} \\ -\frac{1}{2}x^2 + c &= \frac{\hbar}{m\omega}\ln\phi_0(x) && \text{rearrange} \\ -\frac{m\omega}{2\hbar}x^2 + c' &= \ln\phi_0(x) && \text{exponentiate} \\ Ae^{-\frac{m\omega}{2\hbar}x^2} &= \phi_0(x) && \text{normalize} \\ \left(\frac{m\omega}{\hbar\pi}\right)^{\frac{1}{4}}e^{-\frac{m\omega}{2\hbar}x^2} &= \phi_0(x) && \text{with } \alpha = \frac{m\omega}{\hbar}\end{aligned}$$

Integral of a Gaussian:

$$\int_{-\infty}^{\infty} e^{-\frac{1}{2}\alpha x^2} dx = \sqrt{\frac{2\pi}{\alpha}}$$

- What about higher energy states?

$$\begin{aligned}
 \hat{a}^\dagger |0\rangle &= \sqrt{1} |1\rangle \\
 &= \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m\omega}{\hbar}} \hat{X} - i\sqrt{\frac{1}{m\hbar\omega}} \hat{P} \right) |0\rangle && \text{expand} \\
 &= \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m\omega}{\hbar}} x - \sqrt{\frac{\hbar}{m\omega}} \frac{d}{dx} \right) \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha}{2}x^2} && \text{position rep.} \\
 &= \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m\omega}{\hbar}} x - \sqrt{\frac{\hbar}{m\omega}} (-\alpha x) \right) \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha}{2}x^2} && \text{differentiate} \\
 &= \frac{1}{\sqrt{2}} \left(\sqrt{\alpha} x - \frac{1}{\sqrt{\alpha}} (-\alpha x) \right) \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha}{2}x^2} && \text{simplify} \\
 &= \sqrt{2\alpha} \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} x e^{-\frac{\alpha}{2}x^2} && \text{simplify}
 \end{aligned}$$

- Thus, $\phi_1(x)$ is a gaussian times a polynomial
- Repeated application of \hat{a}^\dagger will generate higher energy excited states of the form

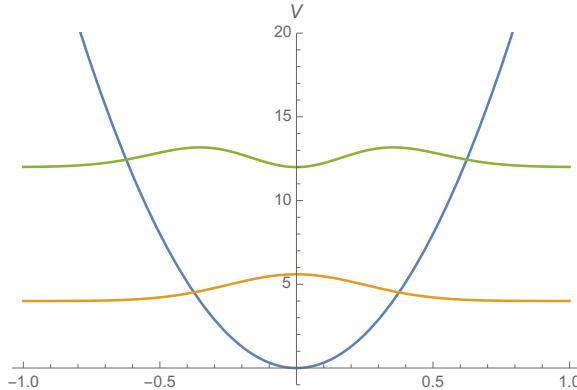
$$\langle x|n\rangle = \phi_n(x) = \frac{N_n}{\sqrt{2^n n!}} H_n(\sqrt{\alpha}x) e^{-\frac{\alpha}{2}x^2}$$

where, H_n are the **Hermite polynomials**, and N_n are the normalization constants

$$\begin{aligned}
 H_0(z) &= 1 \\
 H_1(z) &= 2z \\
 H_2(z) &= 4z^2 - 2
 \end{aligned}$$

⋮

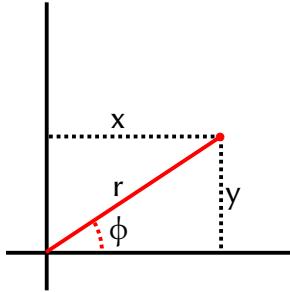
$$H_n(z) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}$$



4 Rotational motion

4.1 Particle in a Ring

- Polar coordinates



- conversions

$$x = r \cos \phi$$

$$y = r \sin \phi$$

$$r = \sqrt{x^2 + y^2}$$

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} \right)$$

polar coordinates

- If the particle is trapped in a ring of fixed size, then $\frac{\partial}{\partial r} \rightarrow 0$

$$\hat{H} = -\frac{\hbar^2}{2mr^2} \frac{\partial^2}{\partial \phi^2}$$

$$= -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$$

I is rotational inertia

$$\hat{H}\psi(\phi) = E\psi(\phi)$$

- Trial wavefunction:

$$\psi(\phi) = Ae^{i\sqrt{\frac{2IE}{\hbar^2}}\phi} + Be^{-i\sqrt{\frac{2IE}{\hbar^2}}\phi}$$

$$= Ae^{im_l\phi} + Be^{-im_l\phi}$$

$$\text{with } m_l = \sqrt{\frac{2IE}{\hbar^2}}$$

- Periodic boundary condition:

$$\psi(\phi) = \psi(\phi + 2\pi)$$

$$Ae^{im_l\phi} + Be^{-im_l\phi} = Ae^{im_l\phi}e^{im_l2\pi} + Be^{-im_l\phi}e^{-im_l2\pi}$$

- * This can only be true iff

$$e^{\pm im_l 2\pi} = 1$$

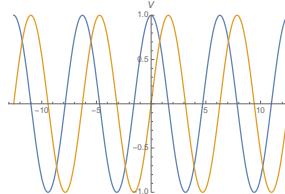
Euler's formula

$$\cos m_l 2\pi \pm i \sin m_l 2\pi = 1$$

- * To make this happen, the sin part must be zero, and the cos part then must be 1

$$m_l 2\pi = 2n\pi \quad \text{for all integers } n$$

$$m_l = \{0, \pm 1, \pm 2, \dots\}$$



- * Thus,

$$E_{m_l} = \frac{m_l^2 \hbar^2}{2I} \quad \forall m_l \in \{0, \pm 1, \pm 2, \dots\}$$

- Wavefunction

- * Since $m_l = 0, \pm 1, \pm 2, \dots$ completely satisfies the boundary conditions, A and B can be anything such that $\psi(\phi)$ can be normalized
- * Set $B = 0$

Note that any other choice would also be a valid decision, i.e.,

$$\psi(\phi) = A' (e^{im_l \phi} + e^{-im_l \phi}) = A' 2 \cos(m_l \phi)$$

- * Normalize

$$\begin{aligned} \int_0^{2\pi} \psi(\phi)^* \psi(\phi) d\phi &= 1 \\ &= |A|^2 \int_0^{2\pi} e^{-im_l \phi} e^{im_l \phi} d\phi \\ &= 2\pi |A|^2 \\ A &= \frac{1}{\sqrt{2\pi}} \\ \psi(\phi) &= \frac{1}{\sqrt{2\pi}} e^{im_l \phi} \end{aligned}$$

- Observations

- * E_{m_l} is discrete and energy levels become more spaced with energy
- * No zero-point energy, $m_l = 0$ is fine! Why is this?

- Angular momentum

- * particle is spinning in a circle, m_l is likely an angular momentum
- * classically, angular momentum is

$$\begin{aligned} l &= \vec{r} \times \vec{p} = \begin{vmatrix} \vec{x} & \vec{y} & \vec{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \\ &= \vec{x}(yp_z - zp_y) + \vec{y}(zp_x - xp_z) + \vec{z}(xp_y - yp_x) \\ &= \vec{x}l_x + \vec{y}l_y + \vec{z}l_z \end{aligned}$$

- * Remember quantum postulate 3? We can replace x and p variables with operators to get the corresponding quantum operators

$$\begin{aligned} \hat{l}_z &= -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) && \text{actually } \langle x | \hat{l}_z | \psi \rangle \\ \hat{l}_z &= -i\hbar \frac{\partial}{\partial \phi} && \text{angular momentum operator} \end{aligned}$$

- * Apply operator to PIR eigenstates

$$\begin{aligned} \hat{l}_z \psi(\phi) &= -i\hbar \frac{\partial}{\partial \phi} \left(\frac{1}{\sqrt{2\pi}} e^{im_l \phi} \right) \\ &= m_l \left(\frac{1}{\sqrt{2\pi}} e^{im_l \phi} \right) \\ &= m_l \left(\frac{1}{\sqrt{2\pi}} e^{im_l \phi} \right) && m_l \text{ is the angular momentum in z-direction} \end{aligned}$$

- * Allowed angular momentum = $\{m_l \hbar = 0, \pm \hbar, \pm 2\hbar, \dots\}$

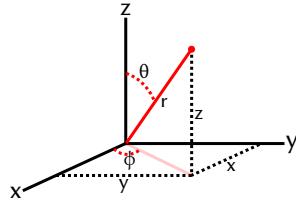
If a different form was chosen

$$\psi(\phi) = A' \left(e^{im_l \phi} + e^{-im_l \phi} \right) = A' 2 \cos(m_l \phi)$$

these are not eigenstates of the \hat{l}_z operator

4.2 Particle on a Sphere

- Spherical coordinates



- Conversions:

$$\begin{aligned}\nabla^2 &= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \\ &= \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2\end{aligned}$$

where,

$$\Lambda^2 = \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta}$$

- A particle on a sphere has a fixed radius, too. Thus,

$$\begin{aligned}\hat{H}\Psi(\theta, \phi) &= \frac{-\hbar^2}{2I} \Lambda^2 \Psi(\theta, \phi) \\ &= \frac{-\hbar^2}{2I} \Lambda^2 \Phi(\phi) \Theta(\theta) && \text{Sep. of Var.} \\ &= E \Phi(\phi) \Theta(\theta) \\ \sin^2 \theta \Lambda^2 \Phi(\phi) \Theta(\theta) &= \left(\frac{\partial^2}{\partial \phi^2} + \sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) \Phi(\phi) \Theta(\theta) && \text{mult. by } \frac{\sin^2 \theta}{-\frac{\hbar^2}{2I}}\end{aligned}$$

- gives

$$\begin{aligned}\left(\frac{\partial^2}{\partial \phi^2} + \sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right) \Phi(\phi) \Theta(\theta) &= -\frac{2IE}{\hbar^2} \sin^2 \theta \Phi(\phi) \Theta(\theta) \\ \Theta \frac{\partial^2}{\partial \phi^2} \Phi &= -\Phi \sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \Theta - \frac{2IE}{\hbar^2} \sin^2 \theta \Phi \Theta \\ \frac{1}{\Phi} \frac{\partial^2}{\partial \phi^2} \Phi &= -\frac{1}{\Theta} \sin \theta \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \Theta - \frac{2IE}{\hbar^2} \sin^2 \theta && \text{Divide by } \Phi \Theta\end{aligned}$$

- $\Phi(\phi)$ is essentially particle in a ring:

$$\begin{aligned}\frac{\partial^2}{\partial \phi^2} \Phi(\phi) &= c \Phi(\phi) \\ \Phi(\phi) &= \frac{1}{\sqrt{2\pi}} e^{im_l \phi} & \forall m_l \in \{0, \pm 1, \pm 2, \dots\}\end{aligned}$$

- Plug this back into the Schrödinger equation:

$$\hat{H}\Phi\Theta = E\Phi\Theta$$

$$\frac{-\hbar^2}{2I} \left[\frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right] \Phi\Theta = E\Phi\Theta$$

$$\frac{-\hbar^2}{2I} \left[\frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right] e^{im_l \phi} \Theta = E e^{im_l \phi} \Theta \quad \text{substitute}$$

$$\frac{-\hbar^2}{2I} \left[\frac{-m_l^2}{\sin^2 \theta} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right] e^{im_l \phi} \Theta = E e^{im_l \phi} \Theta \quad \text{differentiate w.r.t } \phi$$

$$\left[\frac{-m_l^2}{\sin^2 \theta} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{2IE}{\hbar^2} \right] \Theta = 0 \quad \Phi \text{ cancels, and rearrange}$$

- One could then choose to solve this differential equation for $\Theta(\theta)$, we will not. The solutions to this involve the associated Legendre polynomials, P_l :

$$\Theta(\theta) = \left\{ \left(\frac{2l+1}{2} \right) \frac{(l-|m_l|)!}{(l+|m_l|)!} \right\} P_l^{|m_l|}(\cos \theta)$$

- Taken together with the particle in a ring wavefunction, Φ , the final wavefunctions are called **spherical harmonics** $Y_{l,m_l}(\phi, \theta)$

$$Y_{l,m_l} = \Phi(\phi)_{m_l} \Theta(\theta)_{l,m_l}$$

such that

$$\Lambda^2 Y_{lm_l} = -l(l+1)Y_{lm_l} \quad \forall l \in \{0, 1, 2, \dots\}$$

$$\forall m_l \in \{-l, -l+1, \dots, l-1, l\}$$

- this leads to a restriction on the energy levels allowed:

$$E = \frac{l(l+1)\hbar^2}{2I}$$

with, degeneracy

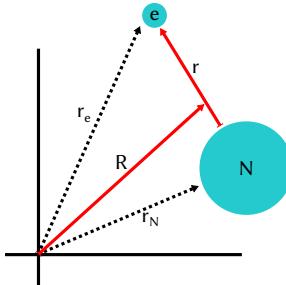
$$g_l = 2l + 1$$

- If we convert the rigid rotor Hamiltonian into spherical coordinates, it is essentially identical to a particle on a sphere. Read about this in Atkins.
- We will come back to this soon...

Start of Lecture 11

4.3 Hydrogen Atom

- Center of mass coordinates



$$\vec{r} = \vec{r}_e - \vec{r}_N$$

$$\vec{R} = \frac{m_e \vec{r}_e + m_N \vec{r}_N}{M}$$

with $M = m_e + m_N$

- we are going to drop the vector arrows...
- Because the coulombic interaction involves both nuclear and electronic degrees of freedom, we cannot use separation of variables, and so we say that the electronic and nuclear degrees of freedom are correlated. In order to simplify our problem, we will find a different set of coordinates which will allow us to apply the separation of variables.
- Hamiltonian in particle coordinates:

$$\hat{H} = \frac{\hat{P}_N^2}{2m_N} + \frac{\hat{P}_e^2}{2m_e} + V(r)$$

- Define new momentum operators: Think of classical mechanics:

$$\begin{aligned}
 \vec{P}_{cm} &= M \vec{V} = M \frac{d}{dt} \vec{R} && \text{"total" momentum} \\
 &= M \frac{d}{dt} \left(\frac{m_e \vec{r}_e + m_N \vec{r}_N}{M} \right) \\
 &= \vec{p}_e + \vec{p}_N \\
 \vec{p} &= \mu \frac{d}{dt} \vec{r} && \text{"internal" momentum} \\
 &= \frac{m_N m_e}{M} \frac{d}{dt} (\vec{r}_e - \vec{r}_N) \\
 &= \frac{m_N m_e}{M} \left(\frac{\vec{p}_e}{m_e} - \frac{\vec{p}_N}{m_N} \right) \\
 &= \frac{m_N \vec{p}_e - m_e \vec{p}_N}{M}
 \end{aligned}$$

$$\hat{P} = \hat{P}_N + \hat{P}_e \quad \text{just sum of the momenta}$$

$$\hat{p} = \frac{m_N \hat{P}_e - m_e \hat{P}_N}{M}$$

Definition: reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

- \hat{P} and \hat{p} commute
- We want to transform the Hamiltonian operator into center-of-mass coordinates
- let's get inverse transformations:

$$\begin{aligned} \hat{p} &= \frac{m_N \hat{P} - m_N \hat{P}_N - m_e \hat{P}_N}{M} && \text{substitute for } \hat{P}_e \\ &= \frac{m_N}{M} \hat{P} - \hat{P}_N && \text{substitute for } \hat{P}_e \end{aligned}$$

so

$$\begin{aligned} \hat{P}_N &= \frac{m_N}{M} \hat{P} - \hat{p} \\ \hat{P}_e &= \frac{m_e}{M} \hat{P} + \hat{p} \end{aligned}$$

- Now substitute into the Hamiltonian

$$\begin{aligned} \hat{H} &= \frac{1}{2m_N} \left(\frac{m_N}{M} \hat{P} - \hat{p} \right)^2 - \frac{1}{2m_e} \left(\frac{m_e}{M} \hat{P} + \hat{p} \right)^2 + V(r) \\ &= \frac{1}{2m_N} \left[\left(\frac{m_N}{M} \hat{P} \right)^2 + \hat{p}^2 - 2 \frac{m_N}{M} \hat{P} \hat{p} \right] + \frac{1}{2m_e} \left[\left(\frac{m_e}{M} \hat{P} \right)^2 + \hat{p}^2 + 2 \frac{m_e}{M} \hat{P} \hat{p} \right] + V(r) \\ &= \frac{1}{2m_N} \left[\left(\frac{m_N}{M} \hat{P} \right)^2 + \hat{p}^2 \right] + \frac{1}{2m_e} \left[\left(\frac{m_e}{M} \hat{P} \right)^2 + \hat{p}^2 \right] + V(r) \\ &= \frac{1}{2} \left[\frac{m_N}{M^2} \hat{P}^2 + \frac{\hat{p}^2}{m_N} + \frac{m_e}{M^2} \hat{P}^2 + \frac{\hat{p}^2}{m_e} \right] + V(r) \\ &= \frac{1}{2} \left[\frac{m_N + m_e}{M^2} \hat{P}^2 + \frac{(m_e + m_N) \hat{p}^2}{m_e m_N} \right] + V(r) \\ &= \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2\mu} + V(r) \end{aligned}$$

- Thus, the Schrödinger equation is separable, and we can now focus only in the internal degrees of freedom

$$\begin{aligned} \left(\frac{\hat{p}^2}{2\mu} - \frac{Ze^2}{4\pi\epsilon_0 r} \right) \psi(r) &= E\psi(r) \\ - \left(\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + \frac{Ze^2}{4\pi\epsilon_0 r} \right) \psi(r) &= E\psi(r) \\ \left(\frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} \Lambda^2 + \frac{Z\mu e^2}{2\hbar^2 \pi \epsilon_0 r} \right) \psi &= \frac{-2\mu E}{\hbar^2} \psi \quad \text{spherical coords} \end{aligned}$$

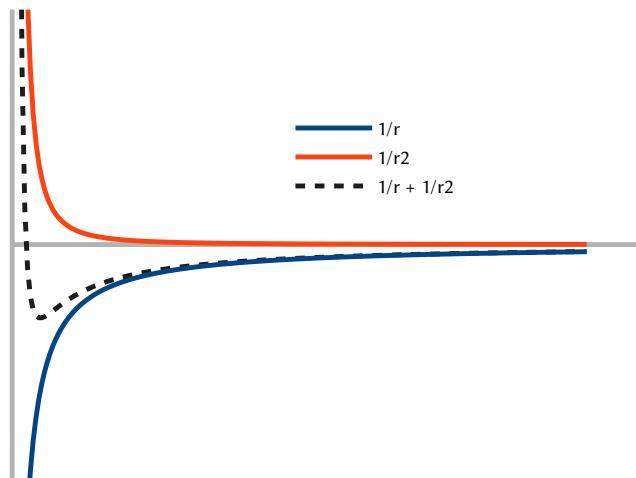
- Assume trial function $\psi(r, \phi, \theta) = R(r)Y_{lm_l}(\phi, \theta)$, with Y being the spherical harmonics

$$\begin{aligned} \left(\frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{1}{r^2} \Lambda^2 + \frac{Z\mu e^2}{2\hbar^2 \pi \epsilon_0 r} \right) RY &= \frac{-2\mu E}{\hbar^2} RY \\ \left(\frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{l(l+1)}{r^2} + \frac{Z\mu e^2}{2\hbar^2 \pi \epsilon_0 r} \right) RY &= \frac{-2\mu E}{\hbar^2} RY \quad \Lambda^2 Y_{lm_l} = -l(l+1) Y_{lm_l} \\ \left(\frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{b}{r^2} + \frac{a}{r} \right) R &= \frac{-2\mu E}{\hbar^2} R \quad \text{simplify, and divide by } Y \\ \left(\frac{\partial^2}{\partial r^2} - \frac{b}{r^2} + \frac{a}{r} \right) u &= \frac{-2\mu E}{\hbar^2} u \quad \text{mult. by } r, \text{ and let } u = Rr \end{aligned}$$

with,

$$\begin{aligned} a &= \frac{2\mu Ze^2}{\hbar^2 4\pi\epsilon_0} \\ b &= l(l+1) \end{aligned}$$

- Notice here that the above equation amounts to solving the Schrödinger equation with an effective Hamiltonian which depends on $l(l+1)$



- Consider long-distance first, limit as $r \rightarrow \infty$:

$$\begin{aligned} \rightarrow \frac{\partial^2}{\partial r^2} u &= \frac{-2\mu E}{\hbar^2} u && \text{as } r \rightarrow \infty \\ u_\infty &= Ae^{i\sqrt{\frac{2\mu|E|}{\hbar^2}}r} + Be^{-i\sqrt{\frac{2\mu|E|}{\hbar^2}}r} \end{aligned}$$

however, we know that $E < 0$, so

$$u_\infty = Ae^{-\sqrt{\frac{2\mu|E|}{\hbar^2}}r} + Be^{\sqrt{\frac{2\mu|E|}{\hbar^2}}r}$$

and to remain square-integrable:

$$\begin{aligned} u_\infty &= Ae^{-\sqrt{\frac{2\mu|E|}{\hbar^2}}r} \\ u_\infty &= Ae^{-\lambda r} && \text{where } \lambda = \sqrt{\frac{2\mu|E|}{\hbar^2}} \end{aligned}$$

- Now what about finite r ?

$$u = u_\infty L(r) \quad \text{with } L(r) = \sum_n c_n r^n$$

does this form make sense? Remember, the exponential will kill off any long-range polynomial tails, due to the relative rates of decay

- Plug it into our original equation, and restricting ourselves again to bound states, such that $-E = |E|$:

$$\begin{aligned} \left(\frac{\partial^2}{\partial r^2} - \frac{b}{r^2} + \frac{a}{r} \right) u &= \lambda^2 u \\ \left(\frac{\partial^2}{\partial r^2} - \frac{b}{r^2} + \frac{a}{r} \right) Le^{-\lambda r} &= \lambda^2 Le^{-\lambda r} && \text{differentiate} \\ \frac{\partial}{\partial r} (L'e^{-\lambda r} - L\lambda e^{-\lambda r}) + \left(-\frac{b}{r^2} + \frac{a}{r} \right) Le^{-\lambda r} &= \lambda^2 Le^{-\lambda r} && \text{differentiate} \\ (L''e^{-\lambda r} - L'\lambda e^{-\lambda r} - L'\lambda e^{-\lambda r} + L\lambda^2 e^{-\lambda r}) + \left(-\frac{b}{r^2} + \frac{a}{r} \right) Le^{-\lambda r} &= \lambda^2 Le^{-\lambda r} \\ L'' - 2L'\lambda + \left(-\frac{b}{r^2} + \frac{a}{r} \right) L &= 0 && \text{simplify} \end{aligned}$$

expand

$$\sum_n c_n n(n-1)r^{n-2} - 2\lambda \sum_n c_n nr^{n-1} - b \sum_n c_n r^{n-2} + a \sum_n c_n r^{n-1} = 0$$

this means

$$\begin{aligned} &\dots + c_n \left[n(n-1)r^{n-2} - 2\lambda nr^{n-1} - br^{n-2} + ar^{n-1} \right] \\ &+ c_{n+1} \left[n(n+1)r^{n-1} - 2\lambda(n+1)r^n - br^{n-1} + ar^n \right] + \dots \\ &= 0 \end{aligned}$$

As a polynomial, for this to generally equal zero, each order of r must also go to zero:

$$\begin{aligned} c_n \left[-2\lambda n r^{n-1} + ar^{n-1} \right] + c_{n+1} \left[n(n+1)r^{n-1} - br^{n-1} \right] &= 0 \\ c_n [-2\lambda n + a] + c_{n+1} [n(n+1) - b] &= 0 \\ c_{n+1} &= \frac{2\lambda n - a}{n(n+1) - b} c_n \end{aligned}$$

- The polynomials defined by these coefficients are called **Laguerre polynomials** to ensure square-integrability, there must be some c_n such that $c_{n+1} = 0$. Another reason, is that since at finite values of r the wavefunction is primarily L , an arbitrarily large n will lead to an arbitrarily large kinetic energy. Our expectation of a finite energy leads to:

$$\begin{aligned} 2\lambda n &= a \\ 2\sqrt{\frac{2\mu|E|}{\hbar^2}} n &= \frac{2\mu}{\hbar^2} \frac{Ze^2}{4\pi\epsilon_0} && \text{substitute} \\ |E| &= \frac{\mu}{n^2\hbar^2} \frac{Z^2e^4}{32\pi^2\epsilon_0^2} && \text{rearrange} \end{aligned}$$

Start of Lecture 12

5 Angular momentum

5.1 Operators

- Classical Angular momentum:

$$\begin{aligned} l &= \vec{r} \times \vec{p} = \begin{vmatrix} \vec{x} & \vec{y} & \vec{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \\ &= \vec{x}(yp_z - zp_y) + \vec{y}(zp_x - xp_z) + \vec{z}(xp_y - yp_x) \\ &= \vec{x}l_x + \vec{y}l_y + \vec{z}l_z \end{aligned}$$

- Quantum postulate: swap dynamical position and momentum variables with operators

$$\begin{aligned}\hat{l}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{l}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{l}_z &= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x\end{aligned}$$

- Magnitude of angular momentum:

$$\hat{\mathbf{l}}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2$$

- angular momentum commutation relations (remember, $[q, p_{q'}] = i\hbar\delta_{q,q'}$):

$$\begin{aligned} [\hat{l}_x, \hat{l}_y] &= [yp_z - zp_y, zp_x - xp_z] \\ &= [yp_z, zp_x] + [zp_y, xp_z] \\ &= yp_x[p_z, z] + xp_y[z, p_z] \\ &= i\hbar\hat{l}_z \\ [\hat{l}_y, \hat{l}_z] &= i\hbar\hat{l}_x \\ [\hat{l}_z, \hat{l}_x] &= i\hbar\hat{l}_y \end{aligned}$$

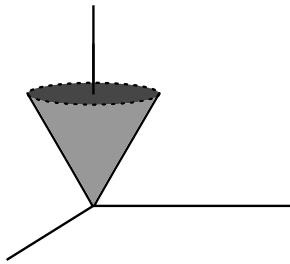
$$\begin{aligned} [\hat{\mathbf{l}}^2, \hat{l}_z] &= [\hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2, \hat{l}_z] = 0 \\ &= [\hat{l}_x^2 + \hat{l}_y^2, \hat{l}_z] \\ &= \hat{l}_x\hat{l}_x\hat{l}_z - \hat{l}_z\hat{l}_x\hat{l}_x + \hat{l}_y\hat{l}_y\hat{l}_z - \hat{l}_z\hat{l}_y\hat{l}_y \\ &= \hat{l}_x(\hat{l}_z\hat{l}_x - i\hbar\hat{l}_y) - \hat{l}_z\hat{l}_x\hat{l}_x + \hat{l}_y(\hat{l}_z\hat{l}_y + i\hbar\hat{l}_x) - \hat{l}_z\hat{l}_y\hat{l}_y \\ &= [\hat{l}_x, \hat{l}_z]\hat{l}_x - i\hbar\hat{l}_x\hat{l}_y + [\hat{l}_y, \hat{l}_z]\hat{l}_y + i\hbar\hat{l}_y\hat{l}_x \\ &= -i\hbar\hat{l}_y\hat{l}_x - i\hbar\hat{l}_x\hat{l}_y + i\hbar\hat{l}_x\hat{l}_y + i\hbar\hat{l}_y\hat{l}_x \\ &= 0 \end{aligned}$$

and the same for \hat{l}_x and \hat{l}_y ,

$$[\hat{\mathbf{l}}^2, \hat{l}_x] = [\hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2, \hat{l}_x] = 0$$

$$[\hat{\mathbf{l}}^2, \hat{l}_y] = [\hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2, \hat{l}_y] = 0$$

- We can only know the angular momentum in one direction at a time. And this can be simultaneously known with the total magnitude, $\hat{\mathbf{l}}^2$
- This suggests a vector model of angular momentum



- Since we can only know one of \hat{l}_x , \hat{l}_y , or \hat{l}_z , at a given time, we will choose one coordinate as the known coordinate, this will be \hat{l}_z .
- angular momentum ladder operators

$$\hat{l}_+ = \hat{l}_x + i\hat{l}_y$$

$$\hat{l}_- = \hat{l}_x - i\hat{l}_y$$

- Note: If we would have picked a different coordinate (not \hat{l}_z) these operators would look a bit different but have the same behavior.
- Consider their commutators on various operators

$$[\hat{l}_z, \hat{l}_+] = [\hat{l}_z, \hat{l}_x + i\hat{l}_y]$$

$$= [\hat{l}_z, \hat{l}_x] + i[\hat{l}_z, \hat{l}_y]$$

$$= i\hbar\hat{l}_y + \hbar\hat{l}_x$$

$$= \hbar\hat{l}_+$$

$$[\hat{l}_z, \hat{l}_-] = -\hbar\hat{l}_-$$

– and

$$[\hat{l}_+, \hat{l}_-] = [\hat{l}_x + i\hat{l}_y, \hat{l}_x - i\hat{l}_y]$$

$$= -i[\hat{l}_x, \hat{l}_y] + i[\hat{l}_y, \hat{l}_x]$$

$$= -2i[\hat{l}_x, \hat{l}_y]$$

$$= 2\hbar\hat{l}_z$$

– and

$$[\hat{\mathbf{l}}^2, \hat{l}_+] = [\hat{\mathbf{l}}^2, \hat{l}_x + i\hat{l}_y]$$

$$= 0 \quad \hat{\mathbf{l}}^2 \text{ commutes with both } \hat{l}_x, \hat{l}_y$$

$$[\hat{\mathbf{l}}^2, \hat{l}_-] = 0$$

- Let us introduce a basis $|\lambda, m_l\rangle$, the eigenstates of $\hat{\mathbf{l}}^2$ and \hat{l}_z (which share eigenvectors, since they commute):

$$\begin{aligned}\hat{\mathbf{l}}^2 |\lambda, m_l\rangle &= \lambda \hbar^2 |\lambda, m_l\rangle \\ \hat{l}_z |\lambda, m_l\rangle &= m_l \hbar |\lambda, m_l\rangle\end{aligned}$$

\hbar has units of angular momentum: $J \cdot s = \text{mass} \cdot \text{length}^2 / \text{time}$

- λ and m_l are related

$$\begin{aligned}\hat{\mathbf{l}}^2 - \hat{l}_z^2 &= \hat{l}_x^2 + \hat{l}_y^2 \\ \langle \lambda, m_l | \hat{\mathbf{l}}^2 - \hat{l}_z^2 | \lambda, m_l \rangle &= \langle \lambda, m_l | \hat{l}_x^2 + \hat{l}_y^2 | \lambda, m_l \rangle \geq 0 && \text{sum of squares of Hermitian operators} \\ &= \hbar^2 (\lambda - m_l^2) \geq 0 \\ \lambda &\geq m_l^2 && \text{important}\end{aligned}$$

- Effect of \hat{l}_+ and \hat{l}_-

$$\begin{aligned}\hat{l}_+ |\lambda, m_l\rangle &= |k\rangle \\ \hat{\mathbf{l}}^2 \hat{l}_+ |\lambda, m_l\rangle &= \hat{l}_+ \hat{\mathbf{l}}^2 |\lambda, m_l\rangle && \text{since } [\hat{\mathbf{l}}^2, \hat{l}_+] = 0 \\ &= \hbar^2 \lambda \hat{l}_+ |\lambda, m_l\rangle && \text{so it is still e'vector of } \hat{\mathbf{l}}^2 \\ \hat{l}_z \hat{l}_+ |\lambda, m_l\rangle &= (\hat{l}_+ \hat{l}_z + \hbar \hat{l}_+) |\lambda, m_l\rangle && \text{since } [\hat{l}_z, \hat{l}_+] = \hbar \hat{l}_+ \\ &= \hbar (m_l + 1) \hat{l}_+ |\lambda, m_l\rangle\end{aligned}$$

so,

$$\begin{aligned}\hat{l}_+ |\lambda, m_l\rangle &\propto |\lambda, m_l + 1\rangle \\ \hat{l}_- |\lambda, m_l\rangle &\propto |\lambda, m_l - 1\rangle\end{aligned}$$

- Now, let's find the proportionality constants for the raising operators acting on an eigenket of $\hat{\mathbf{l}}^2$ and \hat{l}_z , $\hat{l}_+ |\lambda, m_l\rangle = \hbar c_+(\lambda, m_l) |\lambda, m_l + 1\rangle$

- Start with

$$\begin{aligned}\hat{l}_- \hat{l}_+ |\lambda, m_l\rangle &= \hat{l}_- c_+(\lambda, m_l) \hbar |\lambda, m_l + 1\rangle \\ &= c_+(\lambda, m_l) c_-(\lambda, m_l + 1) \hbar^2 |\lambda, m_l\rangle\end{aligned}$$

- also,

$$\begin{aligned}\hat{l}_- \hat{l}_+ |\lambda, m_l\rangle &= (\hat{\mathbf{l}}^2 - \hat{l}_z^2 - \hbar \hat{l}_z) |\lambda, m_l\rangle \\ &= \hbar^2 (\lambda - m_l^2 - m_l) |\lambda, m_l\rangle\end{aligned}$$

– so,

$$c_+(\lambda, m_l) c_-(\lambda, m_l + 1) = \lambda - m_l^2 - m_l$$

– however,

$$\begin{aligned} \langle \lambda, m_l | \hat{l}_- | \lambda, m_l + 1 \rangle^* &= \langle \lambda, m_l + 1 | \hat{l}_+ | \lambda, m_l \rangle \\ c_-(\lambda, m_l + 1)^* &= c_+(\lambda, m_l) \end{aligned}$$

– now, substitute

$$\begin{aligned} c_+(\lambda, m_l) c_+(\lambda, m_l)^* &= |c_+(\lambda, m_l)|^2 \\ &= \lambda - m_l^2 - m_l \end{aligned}$$

$$\begin{aligned} c_+(\lambda, m_l) &= \sqrt{\lambda - m_l(m_l + 1)} && \text{implies choice of phase} \\ c_-(\lambda, m_l) &= \sqrt{\lambda - m_l(m_l - 1)} && \text{by analogous manipulations} \end{aligned}$$

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- Ladder operators lead to relate λ and m_l

– Let m_l assume its maximal value, m_l^{\max} , remembering that $\sqrt{\lambda} \geq |m_l|$

$$\begin{aligned} \hat{l}_+ |\lambda, m_l^{\max}\rangle &= 0 && \text{since this is maximal value of } m_l \\ \hat{l}_- \hat{l}_+ |\lambda, m_l^{\max}\rangle &= 0 && \text{we can do this} \\ (\hat{l}_x - i\hat{l}_y)(\hat{l}_x + i\hat{l}_y) |\lambda, m_l^{\max}\rangle &= 0 && \text{substitute} \\ (\hat{l}_x^2 + \hat{l}_y^2 + i[\hat{l}_x, \hat{l}_y]) |\lambda, m_l^{\max}\rangle &= 0 && \text{expand} \\ (\hat{l}_x^2 + \hat{l}_y^2 - \hbar\hat{l}_z) |\lambda, m_l^{\max}\rangle &= 0 \\ (\hat{\mathbf{l}}^2 - \hat{l}_z^2 - \hbar\hat{l}_z) |\lambda, m_l^{\max}\rangle &= 0 && \text{put in terms of good variables} \\ (\hbar^2\lambda - \hbar^2(m_l^{\max})^2 - \hbar^2m_l^{\max}) |\lambda, m_l^{\max}\rangle &= 0 && \text{eigenvalues} \end{aligned}$$

– For this to be true, regardless of the values of λ , $m_l^{\max} \neq \sqrt{\lambda}$, but rather

$$\lambda = m_l^{\max}(m_l^{\max} + 1) \quad (127)$$

– let us give a label, $l = m_l^{\max}$, to this quantum number such that:

$$\hat{\mathbf{l}}^2 |\lambda, m_l\rangle = l(l+1)\hbar^2 |\lambda, m_l\rangle \quad (128)$$

– we can now replace λ with a value l indicating angular momentum, $|\lambda, m_l\rangle \rightarrow |l, m_l\rangle$

5.2 Quantization of angular momentum

- Now, let us show that both l and m_l are quantized

– Consider both $\hat{l}_+ |l, m_l\rangle$ and $\hat{l}_- |l, m_l\rangle$:

$$\langle l, m_l | \hat{l}_- \hat{l}_+ | l, m_l \rangle = |\hat{l}_+ |l, m_l\rangle|^2 \geq 0 \quad \text{norm squared}$$

$$\langle l, m_l | \hat{l}_+ \hat{l}_- | l, m_l \rangle = |\hat{l}_- |l, m_l\rangle|^2 \geq 0$$

$$\begin{aligned} \hat{l}_- \hat{l}_+ &= (\hat{l}_x - i\hat{l}_y)(\hat{l}_x + i\hat{l}_y) \\ &= \hat{\mathbf{l}}^2 - \hat{l}_z^2 - \hbar \hat{l}_z \\ \hat{l}_+ \hat{l}_- &= (\hat{l}_x + i\hat{l}_y)(\hat{l}_x - i\hat{l}_y) \\ &= \hat{\mathbf{l}}^2 - \hat{l}_z^2 + \hbar \hat{l}_z \end{aligned}$$

– Requiring both $\hat{l}_+ |l, m_l\rangle$ and $\hat{l}_- |l, m_l\rangle$ to have non-negative squared norms, leads to two simultaneous inequalities:

$$\begin{aligned} \langle l, m_l | \hat{l}_- \hat{l}_+ | l, m_l \rangle &= \langle l, m_l | \hat{\mathbf{l}}^2 - \hat{l}_z^2 - \hbar \hat{l}_z | l, m_l \rangle \geq 0 \\ \langle l, m_l | \hat{l}_+ \hat{l}_- | l, m_l \rangle &= \langle l, m_l | \hat{\mathbf{l}}^2 - \hat{l}_z^2 + \hbar \hat{l}_z | l, m_l \rangle \geq 0 \end{aligned}$$

$$\begin{aligned} \hbar^2 (l(l+1) - m_l^2 - m_l) &\geq 0 \\ \hbar^2 (l(l+1) - m_l^2 + m_l) &\geq 0 \end{aligned}$$

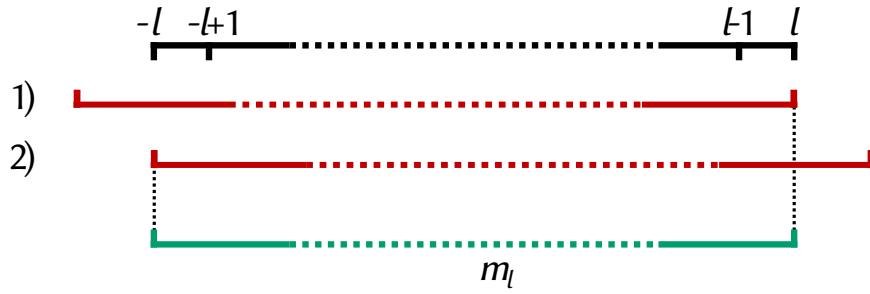
– rearranging:

$$\begin{aligned} l(l+1) - m_l^2 - m_l &= l^2 + l - m_l^2 - m_l \\ &= (l - m_l)(l + m_l) + l - m_l \quad \text{factoring difference of squares} \\ &= (l - m_l)(l + m_l + 1) \end{aligned}$$

$$l(l+1) - m_l^2 + m_l = (l - m_l + 1)(l + m_l) \quad \text{likewise}$$

– since these must be term-wise non-negative:

$$\begin{aligned} -(l+1) &\leq m_l \leq l \\ -l &\leq m_l \leq l+1 \end{aligned}$$



- thus, $-l \leq m_l \leq l$
- In order for all of these results to be true, the distance between $-l$ and l ($2l$) must be an integer. The reason this must be so, is that \hat{l}_- acting on the minimum value must equal 0, and \hat{l}_+ acting on the max value must equal 0. If $2l$ was not an integer, then repeated application of $\hat{l}_+ |l, -l\rangle$ would ultimately lead to states with $m_l > l$. Thus,

$$2l = n \quad \forall n \in \mathbb{I}$$

$$l = \{0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots\}$$

5.3 Spherical Harmonics

- To do this, we now move into the position representation (in spherical polar coordinates)

$$\begin{aligned}\hat{l}_x &= i\hbar \left(\sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \\ \hat{l}_y &= -i\hbar \left(\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \\ \hat{l}_z &= -i\hbar \frac{\partial}{\partial \phi}\end{aligned}$$

derive \hat{l}_+ and \hat{l}_- :

$$\begin{aligned}\hat{l}_+ &= \hbar \left(i \sin \phi \frac{\partial}{\partial \theta} + i \cot \theta \cos \phi \frac{\partial}{\partial \phi} + \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \\ &= \hbar \left((\cos \phi + i \sin \phi) \frac{\partial}{\partial \theta} + i \cot \theta (\cos \phi + i \sin \phi) \frac{\partial}{\partial \phi} \right) \\ &= \hbar e^{i\phi} \left(\frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right)\end{aligned}$$

$$\hat{l}_- = -\hbar e^{-i\phi} \left(\frac{\partial}{\partial \theta} - i \cot \theta \frac{\partial}{\partial \phi} \right)$$

- PS. remember, these are really the position representations of the general operators

$$\hat{l}_z \Rightarrow \langle r | \hat{l}_z | l, m_l \rangle = -i\hbar \frac{\partial}{\partial \phi} Y(\phi, \theta)$$

- Consider \hat{l}_+ acting on maximum m_l state:

$$\begin{aligned}\hat{l}_+ |l, l\rangle &= 0 \\ \hbar e^{i\phi} \left(\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right) Y_{l,l} &= 0 \\ \tan\theta \frac{\partial}{\partial\theta} Y_{l,l} &= -i \frac{\partial}{\partial\phi} Y_{l,l}\end{aligned}$$

- This equation is separable, so let $Y_{ll} = \Phi\Theta$

$$\begin{aligned}\Phi \tan\theta \frac{\partial}{\partial\theta} \Theta &= -i\Theta \frac{\partial}{\partial\phi} \Phi \\ \frac{1}{\Theta} \tan\theta \frac{\partial}{\partial\theta} \Theta &= \frac{-i}{\Phi} \frac{\partial}{\partial\phi} \Phi = k\end{aligned}$$

- Φ can immediately be written down:

$$\Phi(\phi) = A e^{ik\phi}$$

- To get Θ we just integrate:

$$\begin{aligned}\frac{1}{\Theta} \tan\theta \frac{\partial}{\partial\theta} \Theta &= k \\ \frac{1}{\Theta} \partial\Theta &= k \cot\theta \partial\theta && \text{rearrange} \\ \frac{1}{\Theta} \partial\Theta &= k \frac{\cos\theta}{\sin\theta} \partial\theta \\ \frac{1}{\Theta} \partial\Theta &= k \frac{1}{\sin\theta} \partial(\sin\theta) && \text{rearrange} \\ \ln\Theta + c &= \ln \sin^k\theta && \text{integrate} \\ \Theta &= A \sin^k\theta\end{aligned}$$

- What is k ?

$$\begin{aligned}\hat{l}_z Y &= -i\hbar \frac{\partial}{\partial\phi} \Phi\Theta \\ &= k\hbar\Phi\Theta \\ k &= m_l\end{aligned}$$

- So,

$$Y_{l,l}(\phi, \theta) = N_l \sin^l \theta e^{il\phi}$$

- Normalization leads to:

$$N_l = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)!}{4\pi}}$$

- Examples:

$$\begin{aligned} Y_{00} &= \frac{1}{2\sqrt{\pi}} \\ Y_{11} &= -\frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin \theta e^{i\phi} \\ Y_{22} &= \frac{1}{8}\sqrt{\frac{30}{\pi}} \sin^2 \theta e^{i2\phi} \end{aligned}$$

- What about when $l \neq m_l$?

$$\hat{l}_- |l, l\rangle = \hbar \sqrt{l(l+1) - m_l(m_l-1)} |l, l-1\rangle$$

example: Find Y_{10}

$$\begin{aligned} Y_{10} &= -\sqrt{\frac{1}{2}} e^{-i\phi} \left(\frac{\partial}{\partial \theta} - i \cot \theta \frac{\partial}{\partial \phi} \right) \cdot \left(-\frac{1}{2}\sqrt{\frac{3}{2\pi}} \sin \theta e^{i\phi} \right) \\ &= e^{-i\phi} \sqrt{\frac{1}{2}} \sqrt{\frac{3}{8\pi}} (\cos \theta e^{i\phi} - i \cos \theta (i) e^{i\phi}) \\ &= \sqrt{\frac{3}{4\pi}} \cos \theta \end{aligned}$$

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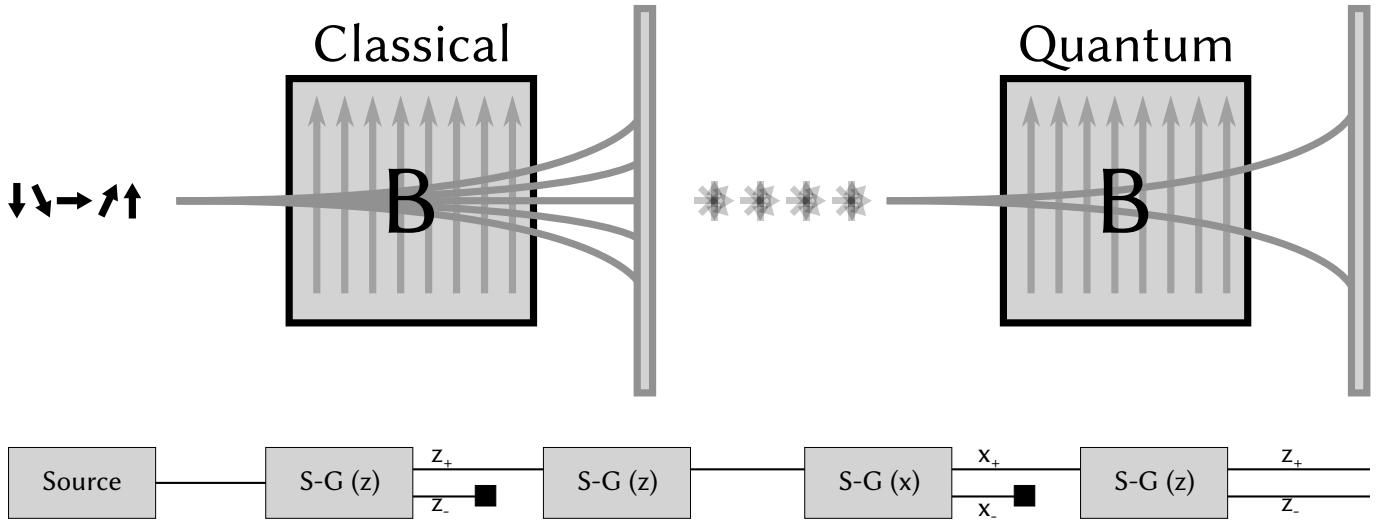
5.4 Spin

- It turns out, (through no derivation in this class) that elementary particles exhibit spatial quantization of an intrinsic angular momentum called “spin”
 - Fermions (including electrons) have an intrinsic angular momentum which has only half-integer values
 - Bosons (including photons) have an intrinsic angular momentum which has only integer values
 - Stern-Gerlach experiment
- In general, different sources of angular momentum have different notations:

\hat{l}_z	orbital angular momentum
\hat{S}_z	intrinsic spin angular momentum
\hat{J}_z	arbitrary angular momentum

- While it might appear like there are simply two kinds of particles, spin-up and spin-down particles, this is not the case. In other words, if we split the particles into two channels with a magnetic field, and block off one of these channels (say, spin-down), we do not observe a “filtering” of the kinds of particles. We can recover the spin-down signal by passing it through perpendicular magnetic fields first!

$$F_z = -\frac{\partial U}{\partial z} = \mu_z \frac{\partial B_z}{\partial z} \quad (129)$$



- Choosing a basis

- we can choose as our basis, either eigenvectors of (\hat{S}^2, \hat{S}_z) or (\hat{S}^2, \hat{S}_x) or (\hat{S}^2, \hat{S}_y) ,
- we will denote these different bases as:

$$\begin{aligned}\hat{S}_x |\pm x\rangle &= \frac{\pm \hbar}{2} |\pm x\rangle \\ \hat{S}_y |\pm y\rangle &= \frac{\pm \hbar}{2} |\pm y\rangle \\ \hat{S}_z |\pm z\rangle &= \frac{\pm \hbar}{2} |\pm z\rangle \\ \hat{S}^2 |\pm \bullet\rangle &= s(s+1)\hbar^2 |\pm \bullet\rangle\end{aligned}$$

- We are able to assume this shorthand notation for spin, because fermions always have $s = \frac{1}{2}$, so

$$|s, m_s\rangle = \left| \frac{1}{2}, m_s \right\rangle \quad (130)$$

contains the unnecessary specification of s .

- Let us again take z to be our preferred direction, and work the eigenvectors of (\hat{S}^2, \hat{S}_z) , with the positive and negative states,

- Since Fermions are defined as having a single value for $s = \frac{1}{2}$, this restricts $m_s = \pm\frac{\hbar}{2}$, and a particle's full state space can be written in a basis of one positive (α) and one negative (β) spin vector

$$\left| \frac{1}{2}, \frac{1}{2} \right\rangle = |z+\rangle = |\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\left| \frac{1}{2}, -\frac{1}{2} \right\rangle = |z-\rangle = |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

- Resolution of identity

$$\mathbf{I} = |\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

- Spin operators in the $\{|\alpha\rangle, |\beta\rangle\}$ basis

- What do the spin operators look like in this basis?

$$\mathbf{I}\hat{S}_z\mathbf{I} = (|\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|) \hat{S}_z (|\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|)$$

$$= \frac{\hbar}{2} |\alpha\rangle\langle\alpha| - \frac{\hbar}{2} |\beta\rangle\langle\beta|$$

$$= \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$= \frac{\hbar}{2} \sigma_z$$

where σ_z is the Pauli matrix for \hat{S}_z

- Likewise

$$\hat{S}^2 = \hbar^2 s(s+1) |\alpha\rangle\langle\alpha| + \hbar^2 s(s+1) |\beta\rangle\langle\beta|$$

$$= \frac{3\hbar^2}{4} \mathbf{I}$$

- Before trying to find \hat{S}_x and \hat{S}_y , let's remember that

$$\begin{aligned}\hat{S}_+ |\beta\rangle &= \hbar \sqrt{s(s+1) - m_s(m_s+1)} |\alpha\rangle \\ &= \hbar \sqrt{\frac{3}{4} - \left(\frac{-1}{2}\right) \frac{1}{2}} |\alpha\rangle \\ &= \hbar |\alpha\rangle \\ \hat{S}_+ |\alpha\rangle &= 0 \\ \hat{S}_- |\alpha\rangle &= \hbar |\beta\rangle\end{aligned}$$

such that,

$$\begin{aligned}\hat{S}_+ &= (|\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|) \hat{S}_+ (|\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|) \\ &= |\alpha\rangle\langle\alpha| \hat{S}_+ |\beta\rangle\langle\beta| && \text{all other terms} = 0 \\ &= \hbar |\alpha\rangle\langle\beta| \\ &= \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\ \hat{S}_- &= \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}\end{aligned}$$

- Recall that

$$\begin{aligned}\hat{S}_+ &= \hat{S}_x + i\hat{S}_y \\ \hat{S}_- &= \hat{S}_x - i\hat{S}_y\end{aligned}$$

$$\begin{aligned}\hat{S}_x &= \frac{\hat{S}_+ + \hat{S}_-}{2} \\ \hat{S}_y &= \frac{\hat{S}_+ - \hat{S}_-}{2i}\end{aligned}$$

- So simply plugging these in we get

$$\begin{aligned}\hat{S}_x &= \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar}{2} \sigma_x \\ \hat{S}_y &= \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{\hbar}{2} \sigma_y\end{aligned}$$

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5.5 Coupling of Angular Momenta

- The vector space spanned by two sources of angular momenta is the direct product of the spaces spanned by each independently, $\mathcal{V}_1 \otimes \mathcal{V}_2 = \mathcal{V}_3$, with operators acting on \mathcal{V}_3 as:

$$\hat{J}_z = \hat{J}_{1z} \oplus \hat{J}_{2z} = \hat{J}_{1z} \otimes \hat{I} + \hat{I} \otimes \hat{J}_{2z}$$

- It's easily seen that these operators are also angular momenta:

$$[\hat{J}_x, \hat{J}_y] = [\hat{J}_{1x} \oplus \hat{J}_{2x}, \hat{J}_{1y} \oplus \hat{J}_{2y}] = i\hbar \hat{J}_z$$

- The operators that act on \mathcal{V}_3 are thus the sum of the operators

$$\begin{aligned}\hat{J}_z &= \hat{J}_{1z} + \hat{J}_{2z} \\ \hat{\mathbf{J}}^2 &= (\hat{J}_{1x} + \hat{J}_{2x})^2 + (\hat{J}_{1y} + \hat{J}_{2y})^2 + (\hat{J}_{1z} + \hat{J}_{2z})^2 \\ &= \hat{J}_{1x}^2 + \hat{J}_{2x}^2 + \hat{J}_{1y}^2 + \hat{J}_{2y}^2 + \hat{J}_{1z}^2 + \hat{J}_{2z}^2 + 2\hat{J}_{1x}\hat{J}_{2x} + 2\hat{J}_{1y}\hat{J}_{2y} + 2\hat{J}_{1z}\hat{J}_{2z} \quad [\hat{J}_{1z}, \hat{J}_{2z}] = 0 \\ &= \hat{\mathbf{J}}_1^2 + \hat{\mathbf{J}}_2^2 + 2\hat{J}_{1x}\hat{J}_{2x} + 2\hat{J}_{1y}\hat{J}_{2y} + 2\hat{J}_{1z}\hat{J}_{2z} \\ &= \hat{\mathbf{J}}_1^2 + \hat{\mathbf{J}}_2^2 + 2\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2\end{aligned}$$

- A single source of angular momentum \hat{J}_{1z} operator doesn't commute with total angular momentum:

$$\begin{aligned}[\hat{J}_{1z}, \hat{\mathbf{J}}^2] &= [\hat{J}_{1z}, \hat{\mathbf{J}}_1^2 + \hat{\mathbf{J}}_2^2 + 2\hat{J}_{1x}\hat{J}_{2x} + 2\hat{J}_{1y}\hat{J}_{2y} + 2\hat{J}_{1z}\hat{J}_{2z}] \\ &= [\hat{J}_{1z}, 2\hat{J}_{1x}\hat{J}_{2x} + 2\hat{J}_{1y}\hat{J}_{2y}] \\ &= 2i\hbar (\hat{J}_{1y}\hat{J}_{2x} - \hat{J}_{1x}\hat{J}_{2y}) \\ &\neq 0\end{aligned}$$

- We can specify $\hat{\mathbf{J}}_1^2$, $\hat{\mathbf{J}}_2^2$, and $\hat{\mathbf{J}}^2$ simultaneously:

$$[\hat{\mathbf{J}}^2, \hat{\mathbf{J}}_1^2] = [\hat{\mathbf{J}}^2, \hat{\mathbf{J}}_2^2] = 0 \quad \text{since, each component commutes}$$

- the summed operators are still angular momentum operators, so all the results for we've recently discussed still hold:

$$\begin{aligned}[\hat{\mathbf{J}}^2, \hat{J}_z] &= 0 \\ [\hat{J}_x, \hat{J}_y] &= i\hbar \hat{J}_z\end{aligned}$$

- Thus, we can add \hat{J}_z to our list of simultaneous observables, allowing us to label states of angular momentum as:

$$|j_1, j_2; J, M\rangle$$

coupled picture

where,

$$\begin{aligned}\hat{\mathbf{J}}^2 |j_1, j_2; J, M\rangle &= J(J+1)\hbar^2 |j_1, j_2; J, M\rangle \\ \hat{J}_z |j_1, j_2; J, M\rangle &= M\hbar |j_1, j_2; J, M\rangle \\ \hat{\mathbf{J}}_1^2 |j_1, j_2; J, M\rangle &= j_1(j_1+1)\hbar^2 |j_1, j_2; J, M\rangle \\ \hat{\mathbf{J}}_2^2 |j_1, j_2; J, M\rangle &= j_2(j_2+1)\hbar^2 |j_1, j_2; J, M\rangle\end{aligned}$$

- However, since $[\hat{\mathbf{J}}_1^2, \hat{J}_{1z}] = 0$, $[\hat{\mathbf{J}}_2^2, \hat{J}_{2z}] = 0$, and $[\hat{\mathbf{J}}_1^2, \hat{\mathbf{J}}_2^2] = 0$, $[\hat{J}_{1z}, \hat{J}_{2z}] = 0$

$$|j_1, m_1; j_2; m_2\rangle$$

uncoupled picture

also forms a good basis

- The quantum numbers of the total angular momenta are restricted to:

$$\begin{aligned}J &= j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2| \\ M &= m_{j1} + m_{j2}\end{aligned}$$

this is known as the Clebsch-Gordan series

- To transform from the coupled basis to the uncoupled basis we simply resolve the identity

$$\begin{aligned}|j_1, j_2; J, M\rangle &= \sum_{m_1, m_2} |j_1, m_1; j_2, m_2\rangle \langle j_1, m_1; j_2, m_2| |j_1, j_2; J, M\rangle \\ &= \sum_{m_1, m_2} |j_1, m_1; j_2, m_2\rangle C_{m_1 m_2}^{JM}\end{aligned}$$

where, $C_{m_1 m_2}^{JM}$ are the Clebsch-Gordan coefficients

- Example: for a d^2 electronic configuration, find the Clebsch-Gordan coefficients for $|2, 2; L = 4, M_l = 3\rangle$
 - We want to express $|4, 3\rangle$ in the basis of uncoupled states
 - High m_s state is easy, since $M_l = m_{l1} + m_{l2}$, there is a one-to-one correspondence between the coupled and uncoupled bases for the highest (and lowest) angular momentum state

$$|l_1 = 2, l_2 = 2; L = 4, M_l = 4\rangle = |l_1 = 2, m_{l1} = 2; l_2 = 2, m_{l2} = 2\rangle$$

- The values for l_1 and l_2 never change (both electrons stay inside d orbitals), so we can simplify our notation

$$|4, 4\rangle = |2; 2\rangle$$

- To get $|4,3\rangle$ we can use the ladder operators

$$\hat{l}_- |4,4\rangle = (\hat{l}_{-1} + \hat{l}_{-2}) |2;2\rangle$$

$$\sqrt{8\hbar} |4,3\rangle = 2\hbar (|1;2\rangle + |2;1\rangle)$$

$$|4,3\rangle = \frac{1}{\sqrt{2}} (|1;2\rangle + |2;1\rangle)$$

- this can be continued,

$$|4,2\rangle = \sqrt{\frac{3}{14}} (|0;2\rangle + |2;0\rangle) + \sqrt{\frac{8}{14}} |1;1\rangle$$

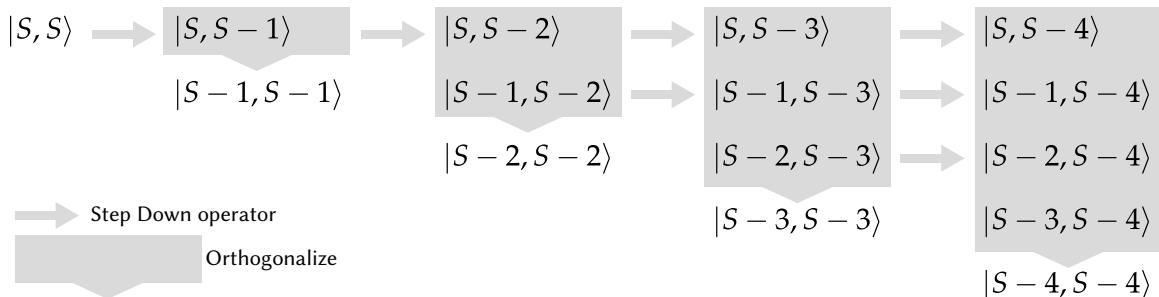
- What about lower angular momentum states like $|3,3\rangle$?

$$|3,3\rangle = a |2;1\rangle + b |1;2\rangle \quad \text{only possibilities to sum to 3}$$

but since states of different angular momentum must be orthogonal, $\langle 4,3|3,3\rangle = 0$

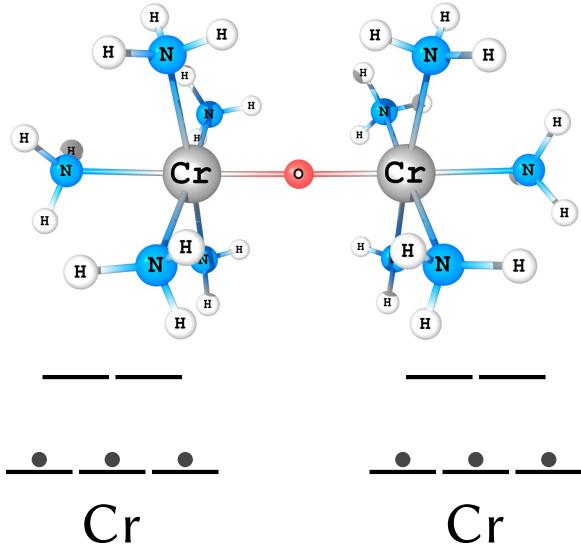
$$\begin{aligned} \langle 4,3|3,3\rangle &= \frac{1}{\sqrt{2}} (\langle 2;1| + \langle 1;2|) (a |2;1\rangle + b |1;2\rangle) \\ &= \frac{1}{\sqrt{2}} (a + b) \quad \text{since } \langle 1;2|2;1\rangle = 0 \\ &= 0 \quad \text{so, } a = -b \\ |3,3\rangle &= \frac{1}{\sqrt{2}} (|2;1\rangle - |1;2\rangle) \quad \text{normalized} \end{aligned}$$

- Basic process



5.6 Dichromium Example

- Consider a real-life example of a transition metal complex:



- Start by focusing on a single Cr atom

- First couple two electrons, then add the third: $s_1 = \frac{1}{2}$ and $s_2 = \frac{1}{2}$

$$S = 1, 0 \quad (131)$$

Possible states for two electrons:

$$|s_1, s_2; S, M_S\rangle \quad \text{Notation reminder} \quad (132)$$

$$\left| \frac{1}{2}, \frac{1}{2}; 1, 1 \right\rangle \quad (133)$$

$$\left| \frac{1}{2}, \frac{1}{2}; 1, 0 \right\rangle \quad (134)$$

$$\left| \frac{1}{2}, \frac{1}{2}; 1, -1 \right\rangle \quad (135)$$

$$\left| \frac{1}{2}, \frac{1}{2}; 0, 0 \right\rangle \quad (136)$$

- For the highest/lowest spin cases, there is only one possible choice for representing these coupled states in the uncoupled basis:

$$\left| \frac{1}{2}, \frac{1}{2}; 1, 1 \right\rangle = |\alpha\rangle |\alpha\rangle \quad (137)$$

$$\left| \frac{1}{2}, \frac{1}{2}; 1, -1 \right\rangle = |\beta\rangle |\beta\rangle \quad (138)$$

- Use \hat{S}_- to get the lower spin states:

$$\hat{S}_- \left| \frac{1}{2}, \frac{1}{2}; 1, 1 \right\rangle = \hbar\sqrt{2} \left| \frac{1}{2}, \frac{1}{2}; 1, 0 \right\rangle \quad (139)$$

$$= (\hat{S}_{-1} + \hat{S}_{-2}) |\alpha\rangle |\alpha\rangle \quad (140)$$

$$= \hbar (|\beta\rangle |\alpha\rangle + |\alpha\rangle |\beta\rangle) \quad (141)$$

revealing,

$$\left| \frac{1}{2}, \frac{1}{2}; 1, 0 \right\rangle = \frac{1}{\sqrt{2}} (\left| \beta \right\rangle \left| \alpha \right\rangle + \left| \alpha \right\rangle \left| \beta \right\rangle) \quad (142)$$

and to ensure orthgonality, $\left\langle \frac{1}{2}, \frac{1}{2}; 0, 0 \middle| \frac{1}{2}, \frac{1}{2}; 1, 0 \right\rangle = 0$,

$$\left| \frac{1}{2}, \frac{1}{2}; 0, 0 \right\rangle = \frac{1}{\sqrt{2}} (\left| \beta \right\rangle \left| \alpha \right\rangle - \left| \alpha \right\rangle \left| \beta \right\rangle) \quad (143)$$

- Now couple both of these spin states to the third electron. How many states are possible?

Case: $s_1 = 1$ and $s_2 = \frac{1}{2}$:

$$S = \frac{3}{2}, \frac{1}{2} \quad \text{Possible spin values} \quad (144)$$

We can easily enumerate all of these coupled states,

$$\left| 1, \frac{1}{2}; \frac{3}{2}, \frac{3}{2} \right\rangle \quad (145)$$

$$\left| 1, \frac{1}{2}; \frac{3}{2}, \frac{1}{2} \right\rangle \quad (146)$$

$$\left| 1, \frac{1}{2}; \frac{3}{2}, -\frac{1}{2} \right\rangle \quad (147)$$

$$\left| 1, \frac{1}{2}; \frac{3}{2}, -\frac{3}{2} \right\rangle \quad (148)$$

$$\left| 1, \frac{1}{2}; \frac{1}{2}, \frac{1}{2} \right\rangle \quad (149)$$

$$\left| 1, \frac{1}{2}; \frac{1}{2}, -\frac{1}{2} \right\rangle \quad (150)$$

Case: $s_1 = 0$ and $s_2 = \frac{1}{2}$:

$$S = \frac{1}{2} \quad \text{Possible spin values} \quad (151)$$

$$\left| 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2} \right\rangle \quad (152)$$

$$\left| 0, \frac{1}{2}; \frac{1}{2}, -\frac{1}{2} \right\rangle \quad (153)$$

- There are two distinct doublet states! $\left| 1, \frac{1}{2}; \frac{1}{2}, M_s \right\rangle$ and $\left| 0, \frac{1}{2}; \frac{1}{2}, M_s \right\rangle$
- Notice that we have identified 8 unique states. Is this the full number of possible spin states? We can check this by combinatorics. Each electron can be in one of two states, and there are three electrons, so the total number of states is $2^3 = 8$ - we've got all of them!

- What do these states look like in the **un-coupled basis**?

There is only one way to obtain $M_s = \frac{3}{2}$, that being $m_{s1} = 1$ and $m_{s2} = \frac{1}{2}$.

So, for the highest spin state, there is a simple one-to-one mapping between the coupled and uncoupled representations.

$$\left| 1, \frac{1}{2}; \frac{3}{2}, \frac{3}{2} \right\rangle = |1, 1\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle \quad (154)$$

- Once again, in order to obtain the non-highest angular momentum states, we will need the ladder operators.

$$\hat{S}_- = \hat{S}_x + i\hat{S}_y \quad (155)$$

$$= (\hat{S}_{x1} + \hat{S}_{x2}) - i(\hat{S}_{y1} + \hat{S}_{y2}) \quad (156)$$

$$= \hat{S}_{-1} + \hat{S}_{-2} \quad (157)$$

$$\hat{S}_- \left| 1, \frac{1}{2}; \frac{3}{2}, \frac{3}{2} \right\rangle = \hbar \sqrt{3} \left| 1, \frac{1}{2}; \frac{3}{2}, \frac{1}{2} \right\rangle \quad (158)$$

$$= (\hat{S}_{-1} + \hat{S}_{-2}) |1, 1\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle \quad (159)$$

$$= \hbar \left(\sqrt{2} |1, 0\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle + |1, 1\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \right) \quad (160)$$

$$\left| 1, \frac{1}{2}; \frac{3}{2}, \frac{1}{2} \right\rangle = \sqrt{\frac{2}{3}} |1, 0\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle + \sqrt{\frac{1}{3}} |1, 1\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \quad (161)$$

$$= \frac{1}{\sqrt{3}} (|\alpha\beta\alpha\rangle + |\beta\alpha\alpha\rangle + |\alpha\alpha\beta\rangle) \quad (162)$$

$$(163)$$

- Now, to find the $\left| 1, \frac{1}{2}; \frac{1}{2}, \frac{1}{2} \right\rangle$ state, we enforce orthogonality again,

$$\left| 1, \frac{1}{2}; \frac{1}{2}, \frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} |1, 0\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle - \sqrt{\frac{2}{3}} |1, 1\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \quad (164)$$

$$= \sqrt{\frac{1}{6}} (|\alpha\beta\alpha\rangle + |\beta\alpha\alpha\rangle) - \sqrt{\frac{2}{3}} |\alpha\alpha\beta\rangle \quad (165)$$

- Now that we have the states on a single Cr atom enumerated, we are now in a position to couple the two Cr atoms together.

- Before we do this, how many states should we expect? A: $2^6 = 64$. Instead of trying to do this, let's focus our attention only on the low-energy states first.
- These Cr atoms have a large energy separation between the $\left| 1, \frac{1}{2}; \frac{3}{2}, M_s \right\rangle$ states and the lower S states. (Just believe me for now). So instead of coupling all states together, if we are interested in enumerating the low energy states, we can restrict our consideration to only the low-energy atomic states (i.e., when $S = \frac{3}{2}$).

- $s_1 = \frac{3}{2}$ and $s_2 = \frac{3}{2}$

$$S = 3, 2, 1, 0 \quad (166)$$

We can easily enumerate all of these coupled states,

$$\left| \frac{3}{2}, \frac{3}{2}; 3, -3 \dots 3 \right\rangle \quad 7 \text{ states : Heptet} \quad (167)$$

$$\left| \frac{3}{2}, \frac{3}{2}; 2, -2 \dots 2 \right\rangle \quad 5 \text{ states : Quintet} \quad (168)$$

$$\left| \frac{3}{2}, \frac{3}{2}; 1, -1 \dots 1 \right\rangle \quad 3 \text{ states : Triplet} \quad (169)$$

$$\left| \frac{3}{2}, \frac{3}{2}; 0, 0 \right\rangle \quad 1 \text{ state : Singlet} \quad (170)$$

- So the low energy spectrum should be comprised of 16 total states among 4 distinct energy levels.

- Energy separation of spin states

- Heisenberg Hamiltonian for calculating the energy of two spins:

$$\hat{H} = -2J\hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2 \quad (171)$$

- Phenomenological model Hamiltonian which assumes that the low energy spectrum is determined by the relative alignments of the two (can be generalized to multiple sites) spins. To see how it separates the different \hat{S}^2 eigenstates let's look at the \hat{S}^2 operator:

$$\hat{S}^2 = (\hat{\vec{S}}_1 + \hat{\vec{S}}_2) \cdot (\hat{\vec{S}}_1 + \hat{\vec{S}}_2) \quad (172)$$

$$= \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2 \quad \text{different sites commute} \quad (173)$$

so,

$$\hat{H} = -J(\hat{S}^2 - \hat{S}_1^2 - \hat{S}_2^2) \quad (174)$$

clearly depends on \hat{S}^2 , \hat{S}_1^2 , \hat{S}_2^2 but not \hat{S}_{1z} or \hat{S}_{2z}

- Heisenberg Hamiltonian is diagonal in the coupled representation:

$$\hat{H} \left| \frac{3}{2}, \frac{3}{2}; 3, M_s \right\rangle = -J\hbar^2 (S(S+1) - S_1(S_1+1) - S_2(S_2+1)) \left| \frac{3}{2}, \frac{3}{2}; 3, M_s \right\rangle \quad (175)$$

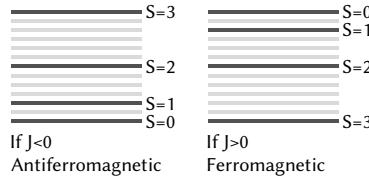
$$= -\frac{9}{2}J\hbar^2 \left| \frac{3}{2}, \frac{3}{2}; 3, M_s \right\rangle \quad (176)$$

$$\hat{H} \left| \frac{3}{2}, \frac{3}{2}; 2, M_s \right\rangle = +\frac{3}{2}J\hbar^2 \left| \frac{3}{2}, \frac{3}{2}; 3, M_s \right\rangle \quad (177)$$

$$\hat{H} \left| \frac{3}{2}, \frac{3}{2}; 1, M_s \right\rangle = +\frac{11}{2}J\hbar^2 \left| \frac{3}{2}, \frac{3}{2}; 3, M_s \right\rangle \quad (178)$$

$$\hat{H} \left| \frac{3}{2}, \frac{3}{2}; 0, 0 \right\rangle = +\frac{15}{2}J\hbar^2 \left| \frac{3}{2}, \frac{3}{2}; 3, M_s \right\rangle \quad (179)$$

- So the energy diagram is:



- What about the uncoupled-basis?

- What does Heisenberg Hamiltonian look like in un-coupled basis: start with operators with clear action on un-coupled states:

$$\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+} = (\hat{S}_{1x} + i\hat{S}_{1y})(\hat{S}_{2x} - i\hat{S}_{2y}) + (\hat{S}_{1x} - i\hat{S}_{1y})(\hat{S}_{2x} + i\hat{S}_{2y}) \quad (180)$$

$$= 2\hat{S}_{1x}\hat{S}_{2x} + 2\hat{S}_{1y}\hat{S}_{2y} \quad (181)$$

$$= 2\hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2 - 2\hat{S}_{1z}\hat{S}_{2z} \quad (182)$$

leading to,

$$\hat{H} = -2J\hat{\vec{S}}_1 \cdot \hat{\vec{S}}_2 = -J(\hat{S}_{1+}\hat{S}_{2-} + \hat{S}_{1-}\hat{S}_{2+} + 2\hat{S}_{1z}\hat{S}_{2z}) \quad (183)$$

- Act \hat{H} on to uncoupled basis to determine matrix elements:

- The high and low spin cases are diagonal, since the only get acted upon by \hat{S}_z

$$\hat{H}|\alpha\alpha\rangle = -2J\hbar^2 \left(\frac{1}{2}\right) \left(\frac{1}{2}\right) |\alpha\alpha\rangle = -\frac{1}{2}J\hbar^2 |\alpha\alpha\rangle \quad (184)$$

$$\hat{H}|\beta\beta\rangle = -2J\hbar^2 \left(-\frac{1}{2}\right) \left(-\frac{1}{2}\right) |\beta\beta\rangle = -\frac{1}{2}J\hbar^2 |\beta\beta\rangle \quad (185)$$

- The $m_s = 0$ cases are not diagonal

$$\hat{H}|\alpha\beta\rangle = -J(\hat{S}_{1+}\hat{S}_{2-}|\alpha\beta\rangle + \hat{S}_{1-}\hat{S}_{2+}|\alpha\beta\rangle + 2\hat{S}_{1z}\hat{S}_{2z}|\alpha\beta\rangle) \quad (186)$$

$$= -J\hbar^2 \left(|\beta\alpha\rangle - \frac{1}{2}|\alpha\beta\rangle\right) \quad (187)$$

- Thus, the Hamiltonian matrix in the basis: $\{|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle\}$ is:

$$\mathbf{H} = -J\hbar^2 \begin{pmatrix} & |\alpha\alpha\rangle & |\alpha\beta\rangle & |\beta\alpha\rangle & |\beta\beta\rangle \\ \hline \langle\alpha\alpha| & \frac{1}{2} & 0 & 0 & 0 \\ \langle\alpha\beta| & 0 & -\frac{1}{2} & 1 & 0 \\ \langle\beta\alpha| & 0 & 1 & -\frac{1}{2} & 0 \\ \langle\beta\beta| & 0 & 0 & 0 & \frac{1}{2} \end{pmatrix} \quad (188)$$

- Eigenvalues:

$$1. -\frac{1}{2}J\hbar^2 : \{|\alpha\alpha\rangle, |\beta\beta\rangle, \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle)\}$$

$$2. \frac{3}{2}J\hbar^2 : \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle)$$

6 Techniques of Approximation

6.1 Time-independent perturbation theory

6.1.1 Two-level system

- Consider a system with only 2 states, $|1\rangle, |2\rangle$ with energies E_1, E_2
- Being eigenstates of \hat{H} , the Hamiltonian in this basis is diagonal:

$$\hat{H} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

- Now, let's add a "small" perturbation to the system, which potentially mixes the two states:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} + \begin{pmatrix} 0 & \epsilon \\ \epsilon & 0 \end{pmatrix} = \begin{pmatrix} E_1 & \epsilon \\ \epsilon & E_2 \end{pmatrix}$$

- Familiar examples:
 - * Harmonic Oscillator: adding αx^3
 - * Heisenberg Hamiltonian: adding magnetic moment
 - * Orbital mixing between atoms
- Kets $|1\rangle$ and $|2\rangle$ are no longer eigenstates
- We want to find the new energies and states of the new Hamiltonian such that $|\psi\rangle = c_1|1\rangle + c_2|2\rangle$
 - We need to solve:

$$\begin{aligned} \hat{H}|\psi\rangle &= E|\psi\rangle \\ (\hat{H} - \mathbf{I}E)|\psi\rangle &= 0 \\ \begin{pmatrix} E_1 - E & \epsilon \\ \epsilon & E_2 - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} &= 0 \end{aligned}$$

- If $(\hat{H} - \mathbf{I}E)^{-1}$ exists, only trivial solution obtained
- To get a non-trivial solution, $(\hat{H} - \mathbf{I}E)^{-1}$ must not exist
- If $\det|\hat{H} - \mathbf{I}E| = 0$, then the inverse doesn't exist

The determinant of a matrix is equal to the product of the eigenvalues. If at least one eigenvalue is zero, then the determinant is zero. If at least one eigenvalue is zero, then the inverse diverges.

- Thus, we seek solutions to the following **secular equation**, by solving for E :

$$\begin{aligned} 0 &= \begin{vmatrix} E_1 - E & \epsilon \\ \epsilon & E_2 - E \end{vmatrix} \\ &= (E_1 - E)(E_2 - E) - \epsilon^2 \\ &= E^2 + (-E_1 - E_2)E + (E_1 E_2 - \epsilon^2) \quad \text{quadratic equation in } E \end{aligned}$$

Remember, quadratic equation :

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

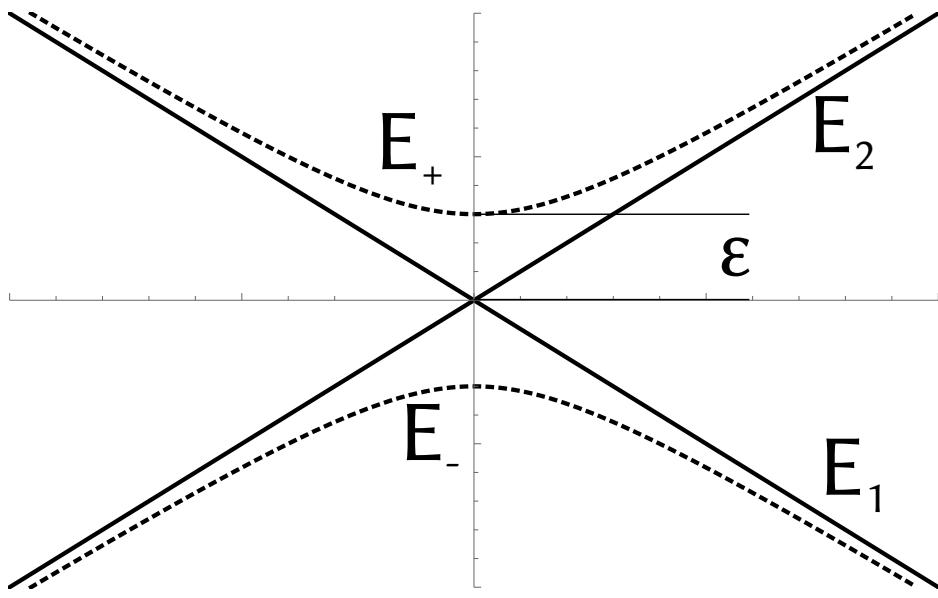
- Two solutions, E_+ and E_-

$$\begin{aligned} E_{\pm} &= \frac{E_1 + E_2}{2} \pm \sqrt{E_1^2 + E_2^2 + 2E_1 E_2 - 4E_1 E_2 + 4\epsilon^2}/2 \\ &= \bar{E} \pm \frac{\sqrt{\Delta E^2 + 4\epsilon^2}}{2} \quad \text{where } \bar{E} = \frac{E_1 + E_2}{2}, \Delta E = E_2 - E_1 \end{aligned}$$

- The perturbation shifts the energies up and down, about the average energy

- Let's inspect this a bit...

- If $\Delta E = 0$, then $E_{\pm} = \bar{E} \pm \epsilon$
- If $\epsilon = 0$, then $E_{\pm} = E_{1,2}$
- Let's plot this as a function of the energy gap of the original (unperturbed) eigenstates ΔE ,



- What about intermediate regions?
- Case 1: $\frac{4\epsilon^2}{\Delta E^2} \ll 1$:
 - First, rearrange

$$E_{\pm} = \bar{E} \pm \frac{1}{2} \Delta E \left(1 + \frac{4\epsilon^2}{\Delta E^2} \right)^{1/2} \quad \text{rearranging}$$

- let's use the **Taylor series** form of $(1 + x)^{1/2} = 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \dots$

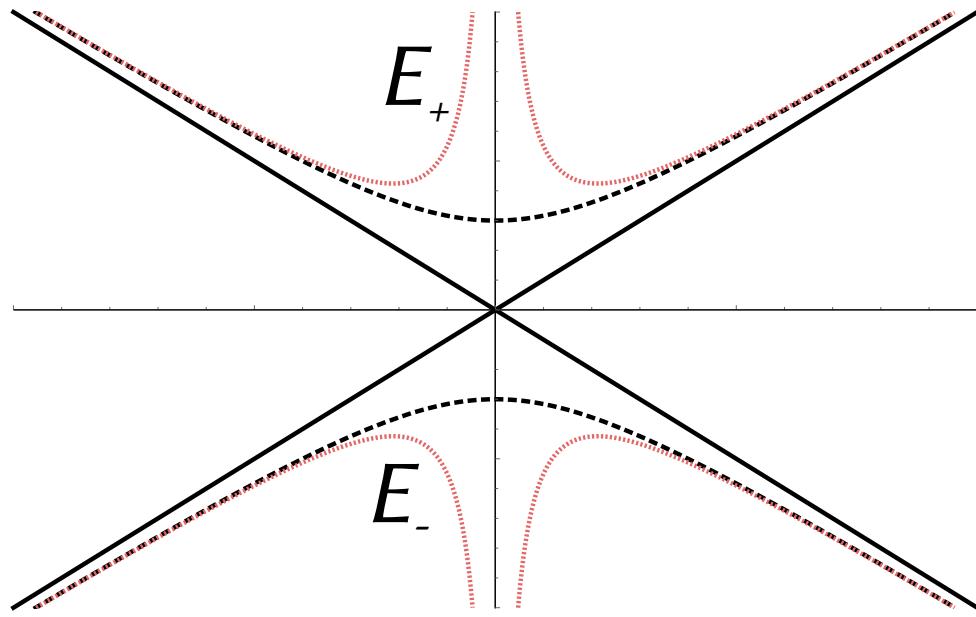
Definition: Taylor series

$$f(x) = \sum_{n=0}^{\infty} \frac{1}{n!} f^{(n)}(0) x^n$$

- plugging this in,

$$\begin{aligned} E_{\pm} &= \bar{E} \pm \frac{1}{2} \Delta E \left[1 + \frac{1}{2} \frac{4\epsilon^2}{\Delta E^2} - \frac{1}{8} \left(\frac{4\epsilon^2}{\Delta E^2} \right)^2 - \dots \right] \\ &\approx \bar{E} \pm \frac{1}{2} \left(\Delta E + 2 \frac{\epsilon^2}{\Delta E} \right) \end{aligned} \quad \text{truncating at first order}$$

- Plotting this...

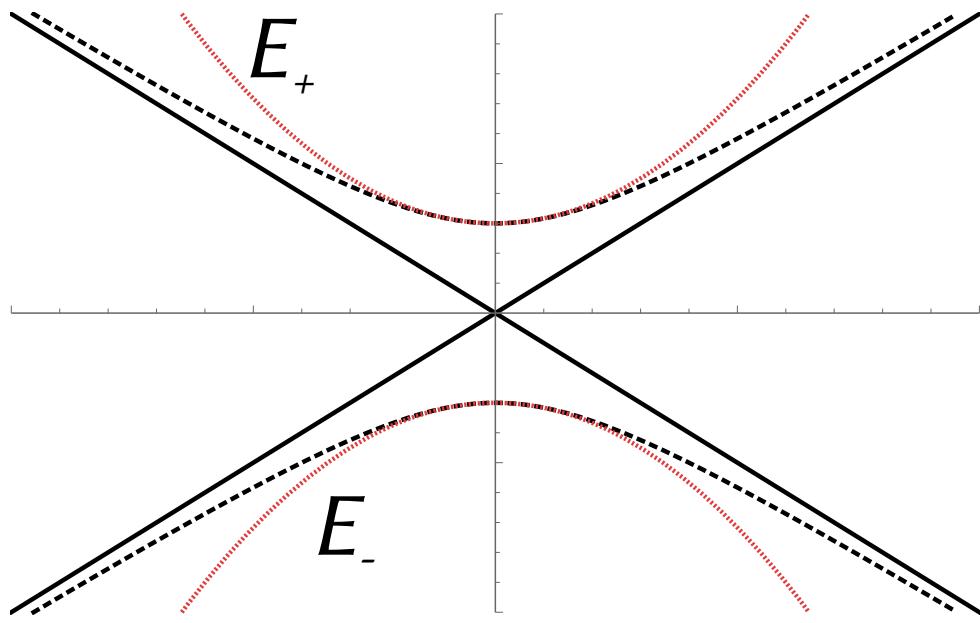


- Good when ΔE is large, but blows up when ΔE goes to zero
- Case 2: $\frac{4\epsilon^2}{\Delta E^2} \gg 1$:

- First, rearrange differently, taking $\frac{\Delta E^2}{4\epsilon^2} = x$

$$\begin{aligned}
 E_{\pm} &= \bar{E} \pm \frac{1}{2} \left[2\epsilon \left(1 + \frac{\Delta E^2}{4\epsilon^2} \right)^{1/2} \right] \\
 &\approx \bar{E} \pm \epsilon \left(1 + \frac{\Delta E^2}{8\epsilon^2} \right) \quad \text{first order} \\
 &\approx \bar{E} \pm \left(\epsilon + \frac{\Delta E^2}{8\epsilon} \right)
 \end{aligned}$$

- this is a quadratic equation in ΔE and can be plotted as such,



6.1.2 Many-level systems

- Many-level systems
 - For a 2-level system, a small perturbation has a quadratic effect on the energies: $\pm \frac{\epsilon^2}{\Delta E}$
 - How do we approach a similar problem when we have a large number (greater than 2) of states?
 - Perturbation theory: We will assume we have a good guess, and the use that guess to construct corrections due to the perturbation
 - We will also assume the energy eigenstates are non-degenerate.

- Start with the Time-independent Schrödinger equation

$$\hat{H} |i\rangle = E |i\rangle$$

- Generally this problem is very hard. Instead of trying to solve it directly, sometimes we can find a very simple Hamiltonian, $\hat{H}^{(0)}$, that is similar to the exact \hat{H} , but whose form is simple enough to permit an exact solution.
- The remainder, $\hat{H}^{(1)}$, is called a perturbation to our unperturbed $\hat{H}^{(0)}$ Hamiltonian such that:

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)}$$

where we have introduced an order-parameter, λ , which will ultimately be set to one. But for now this helps keep track of the significance of terms

- We will also expand our wavefunction and energy in orders of the perturbation strength:

$$\begin{aligned} |i\rangle &= |i^{(0)}\rangle + \lambda |i^{(1)}\rangle + \lambda^2 |i^{(2)}\rangle + \dots \\ E_i &= E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \dots \end{aligned}$$

- Plugging this all into the Schrödinger equation:

$$(\hat{H}^{(0)} + \lambda \hat{H}^{(1)}) (\left| i^{(0)} \right\rangle + \lambda \left| i^{(1)} \right\rangle + \dots) = (E_i^{(0)} + \lambda E_i^{(1)} + \dots) (\left| i^{(0)} \right\rangle + \lambda \left| i^{(1)} \right\rangle + \dots)$$

and collecting orders:

$$\begin{aligned} (\hat{H}^{(0)} - E_i^{(0)}) \left| i^{(0)} \right\rangle &= 0 & : \lambda^0 \\ (\hat{H}^{(0)} - E_i^{(0)}) \left| i^{(1)} \right\rangle + (\hat{H}^{(1)} - E_i^{(1)}) \left| i^{(0)} \right\rangle &= 0 & : \lambda^1 \\ (\hat{H}^{(0)} - E_i^{(0)}) \left| i^{(2)} \right\rangle + (\hat{H}^{(1)} - E_i^{(1)}) \left| i^{(1)} \right\rangle - E_i^{(2)} \left| i^{(0)} \right\rangle &= 0 & : \lambda^2 \\ &\vdots \end{aligned}$$

- Left multiply by $\langle i^{(0)} |$,

$$\begin{aligned} \langle i^{(0)} | (\hat{H}^{(0)} - E_i^{(0)}) \left| i^{(0)} \right\rangle &= 0 & : \lambda^0 \\ \langle i^{(0)} | (\hat{H}^{(0)} - E_i^{(0)}) \left| i^{(1)} \right\rangle + \langle i^{(0)} | (\hat{H}^{(1)} - E_i^{(1)}) \left| i^{(0)} \right\rangle &= 0 & : \lambda^1 \\ \langle i^{(0)} | (\hat{H}^{(0)} - E_i^{(0)}) \left| i^{(2)} \right\rangle + \langle i^{(0)} | (\hat{H}^{(1)} - E_i^{(1)}) \left| i^{(1)} \right\rangle - E_i^{(2)} &= 0 & : \lambda^2 \\ &\vdots \end{aligned}$$

- Simplify,

$$\begin{aligned} 0 &= 0 & : \lambda^0 \\ \langle i^{(0)} | \hat{H}^{(1)} \left| i^{(0)} \right\rangle &= E_i^{(1)} & : \lambda^1 \\ \langle i^{(0)} | (\hat{H}^{(1)} - E_i^{(1)}) \left| i^{(1)} \right\rangle &= E_i^{(2)} & : \lambda^2 \\ &\vdots \end{aligned}$$

- Where does $\left| i^{(1)} \right\rangle$ come from? We will use the zeroth-order states as a basis to represent the perturbed wavefunctions:

$$\left| i^{(1)} \right\rangle = \sum_j c_{ij}^{(1)} \left| j^{(0)} \right\rangle$$

- Substitute this back into expression for $E_i^{(2)}$,

$$\begin{aligned}
 E_i^{(2)} &= \left\langle i^{(0)} \left| \left(\hat{H}^{(1)} - E_i^{(1)} \right) \right| i^{(1)} \right\rangle \\
 &= \sum_j c_{ij}^{(1)} \left\langle i^{(0)} \left| \left(\hat{H}^{(1)} - E_i^{(1)} \right) \right| j^{(0)} \right\rangle \\
 &= \sum_j c_{ij}^{(1)} \left\langle i^{(0)} \left| \hat{H}^{(1)} \right| j^{(0)} \right\rangle - E_i^{(1)} \\
 &= \sum_{j \neq i} c_{ij}^{(1)} \left\langle i^{(0)} \left| \hat{H}^{(1)} \right| j^{(0)} \right\rangle + \left\langle i^{(0)} \left| \hat{H}^{(1)} \right| i^{(0)} \right\rangle - E_i^{(1)} \\
 &= \sum_{j \neq i} c_{ij}^{(1)} \left\langle i^{(0)} \left| \hat{H}^{(1)} \right| j^{(0)} \right\rangle
 \end{aligned}$$

- From where do we get the coefficients? Left multiply the Schrödinger equation for λ^1 by $\left\langle j^{(0)} \right|$, where $j \neq i$,

$$\begin{aligned}
 \left\langle j^{(0)} \left| \left(\hat{H}^{(0)} - E_i^{(0)} \right) \right| i^{(1)} \right\rangle + \left\langle j^{(0)} \left| \left(\hat{H}^{(1)} - E_i^{(1)} \right) \right| i^{(0)} \right\rangle &= 0 & : \lambda^1 \\
 \sum_{k \neq i} \left\langle j^{(0)} \left| \left(\hat{H}^{(0)} - E_i^{(0)} \right) \right| k^{(0)} \right\rangle c_{ik}^{(1)} + \left\langle j^{(0)} \left| \hat{H}^{(1)} \right| i^{(0)} \right\rangle &= 0 \\
 \sum_{k \neq i} \left(E_j^{(0)} - E_i^{(0)} \right) \delta_{jk} c_{ik}^{(1)} + \left\langle j^{(0)} \left| \hat{H}^{(1)} \right| i^{(0)} \right\rangle &= 0 \\
 \left(E_j^{(0)} - E_i^{(0)} \right) c_{ij}^{(1)} + \left\langle j^{(0)} \left| \hat{H}^{(1)} \right| i^{(0)} \right\rangle &= 0 \\
 c_{ij}^{(1)} &= -\frac{\left\langle j^{(0)} \left| \hat{H}^{(1)} \right| i^{(0)} \right\rangle}{E_j^{(0)} - E_i^{(0)}}
 \end{aligned}$$

- We can plug this back into the expression for $E_i^{(2)}$,

$$\begin{aligned}
 E_i^{(2)} &= \sum_{j \neq i} \frac{\left\langle j^{(0)} \left| \hat{H}^{(1)} \right| i^{(0)} \right\rangle \left\langle i^{(0)} \left| \hat{H}^{(1)} \right| j^{(0)} \right\rangle}{E_i^{(0)} - E_j^{(0)}} \\
 &= \sum_{j \neq i} \frac{|H_{ij}^{(1)}|^2}{E_i^{(0)} - E_j^{(0)}}
 \end{aligned}$$

■

- Note the resemblance to the second-order expression for the two-level system,

$$E_{\pm} \approx \bar{E} \pm \left(\frac{\Delta E}{2} + \frac{\epsilon^2}{\Delta E} \right)$$

6.2 Variational Approximation

- Perturbation theory does not provide actual eigenstates of the Hamiltonian. Also, it can blow up in the presence of “accidental” near degeneracies. Think back to the behavior of a 2-level system. Further, it requires us being able to solve an appropriate zeroth order Hamiltonian, which may not always be possible.
- Instead of the perturbative strategy that we just looked at, now consider the Rayleigh ratio :

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

- For any given “trial” wavefunction (one that is not necessarily an exact eigenstate of \hat{H}), the expectation value of the energy is an upper limit to the exact energy of the ground state $|\psi_0\rangle$:

$$\epsilon \geq E_0$$

- To prove this, let us first normalize the trial wavefunction

$$\langle \psi' | \psi' \rangle = 1$$

and then insert the resolution of the identity for the basis of exact energy eigenstates:

$$\begin{aligned} \langle \psi' | \hat{H} | \psi' \rangle &= \sum_{ij} \langle \psi' | \psi_i \rangle \langle \psi_i | \hat{H} | \psi_j \rangle \langle \psi_j | \psi' \rangle && \text{RI} \\ &= \sum_i \langle \psi' | \psi_i \rangle E_i \langle \psi_i | \psi' \rangle && \text{Eigenstates} \\ &= \sum_i E_i |c_i|^2 \geq E_0 \end{aligned}$$

- ϵ is a weighted average of the exact eigenstates, and only equals the true ground state energy when the trial wavefunction has unit overlap with the exact ground state
- Since ϵ is guaranteed to be higher than the exact ground state, we can obtain the best possible wavefunction, by modifying it to yield lower and lower ϵ . We thus variationally optimize the wavefunction to yield the best approximation (for a given trial functional form)
- Choose a wavefunction *ansatz*, by assuming an explicit functional form of the wavefunction
- Linear optimization problems are easier than non-linear: → Rayleigh-Ritz method

- Choose a fixed basis to represent your wavefunction

$$|\psi'\rangle = \sum_i |\phi_i\rangle c_i$$

- Optimize the expansion coefficients, c_i , to minimize the energy. Use Lagrange’s method of undetermined multipliers , and minimize the following objective function:

$$\mathcal{L} = \langle \psi' | \hat{H} | \psi' \rangle - \lambda (\langle \psi' | \psi' \rangle - 1)$$

- This guarantees that the solution obtained will find the lowest energy, provided the wavefunction remains orthonormal

$$\mathcal{L} = \sum_{ij} \langle \phi_i | \hat{H} | \phi_j \rangle c_i c_j - \lambda \left(\sum_i c_i^2 - 1 \right)$$

set the first-derivative of this to zero,

$$\begin{aligned} \frac{\partial}{\partial c_k} \mathcal{L} &= 0 \\ &= \sum_j \langle \phi_k | \hat{H} | \phi_j \rangle c_j + \sum_j \langle \phi_j | \hat{H} | \phi_k \rangle c_j - 2\lambda c_k \\ &= H_{kj} c_j - \lambda c_k = 0 \end{aligned}$$

in matrix form:

$$\mathbf{H}\mathbf{c} = \mathbf{c}\lambda$$

- Thus, when we use a linear parameterization of the wavefunction, we get the energies, λ , and states, \mathbf{c} , by matrix diagonalization

- Hellmann-Feynman theorem

- How does the energy change when a perturbation is applied?
- Assume we have found a variational solution via the Rayleigh-Ritz method

$$\hat{H} |\psi\rangle = E |\psi\rangle$$

- Both the energy and states are functions of the perturbation

$$\begin{aligned} \frac{\partial}{\partial \lambda} \langle \psi | \hat{H} | \psi \rangle &= \left\langle \frac{\partial}{\partial \lambda} \psi \middle| \hat{H} \middle| \psi \right\rangle + \langle \psi | \frac{\partial}{\partial \lambda} \hat{H} | \psi \rangle + \left\langle \psi \middle| \hat{H} \middle| \frac{\partial}{\partial \lambda} \psi \right\rangle \\ &= E \left\langle \frac{\partial}{\partial \lambda} \psi \middle| \psi \right\rangle + \langle \psi | \frac{\partial}{\partial \lambda} \hat{H} | \psi \rangle + E \left\langle \psi \middle| \frac{\partial}{\partial \lambda} \psi \right\rangle \\ &= E \left(\left\langle \frac{\partial}{\partial \lambda} \psi \middle| \psi \right\rangle + \left\langle \psi \middle| \frac{\partial}{\partial \lambda} \psi \right\rangle \right) + \langle \psi | \frac{\partial}{\partial \lambda} \hat{H} | \psi \rangle \\ &= E \frac{\partial}{\partial \lambda} \langle \psi | \psi \rangle + \langle \psi | \frac{\partial}{\partial \lambda} \hat{H} | \psi \rangle && \text{un-chain rule} \\ &= \langle \psi | \frac{\partial}{\partial \lambda} \hat{H} | \psi \rangle && \text{derivative of constant } \blacksquare \end{aligned}$$

6.3 Time-dependent perturbation theory

- Overview:

1. Find eigenstates, $|n\rangle$, of the time-independent Hamiltonian first
2. Express the eigenfunctions of the TDSE as linear combinations of TISE eigenstates, with time-dependent coefficients
3. Solve TDSE by optimizing expansion coefficients

- TDSE:

$$\hat{H} |\Psi(t)\rangle = i\hbar \frac{d}{dt} |\Psi(t)\rangle$$

– Remember, if $\hat{H} \neq f(t)$, then

$$\begin{aligned} |\Psi(t)\rangle &= |\psi\rangle |\phi(t)\rangle \\ &= |\psi\rangle e^{-iEt/\hbar} \\ &= |\Psi^{(0)}(t)\rangle \end{aligned}$$

where the " $^{(0)}$ ", indicates solution of a time-independent zeroth-order Hamiltonian, and

$$\hat{H} |\psi\rangle = E |\psi\rangle \quad \text{TISE}$$

- However, when $\hat{H} = f(t)$, the above is not true
- Let's write the Hamiltonian as a sum of a time-independent part, and a time-dependent operator:

$$\hat{H} = \hat{H}_0 + \hat{V}(t)$$

and use the TISE solutions as a basis:

$$\begin{aligned} |\Psi(t)\rangle &= \sum_n c_n(t) |\Psi_n^{(0)}(t)\rangle \\ &= \sum_n c_n(t) |n\rangle e^{-iE_n t/\hbar} \end{aligned}$$

- Notice, that these states have time dependence in both the coefficient, and the exponential phase part

- Now, let's use the expansion over stationary states for solving the TDSE

$$\begin{aligned} \hat{H} |\Psi(t)\rangle &= i\hbar \frac{d}{dt} |\Psi(t)\rangle \\ (\hat{H}^{(0)} + V(t)) \sum_n c_n(t) |\Psi_n^{(0)}(t)\rangle &= i\hbar \sum_n \dot{c}_n(t) |\Psi_n^{(0)}(t)\rangle + i\hbar \sum_n c_n(t) \frac{d}{dt} |\Psi_n^{(0)}(t)\rangle \\ \hat{H}^{(0)} \sum_n c_n(t) |\Psi_n^{(0)}(t)\rangle + V(t) \sum_n c_n(t) |\Psi_n^{(0)}(t)\rangle &= i\hbar \sum_n \dot{c}_n(t) |\Psi_n^{(0)}(t)\rangle + \hat{H}^{(0)} \sum_n c_n(t) |\Psi_n^{(0)}(t)\rangle \\ V(t) \sum_n c_n(t) |\Psi_n^{(0)}(t)\rangle &= i\hbar \sum_n \dot{c}_n(t) |\Psi_n^{(0)}(t)\rangle \\ V(t) \sum_n c_n(t) |n\rangle e^{-iE_n t/\hbar} &= i\hbar \sum_n \dot{c}_n(t) |n\rangle e^{-iE_n t/\hbar} \end{aligned}$$

Now, multiply by $\langle m |$

$$\langle m | V(t) \sum_n c_n(t) | n \rangle e^{-iE_n t / \hbar} = i\hbar \sum_n \dot{c}_n(t) \langle m | n \rangle e^{-iE_n t / \hbar}$$

$$\frac{1}{i\hbar} \sum_n c_n(t) \langle m | V(t) | n \rangle e^{i\omega_{mn} t} = \dot{c}_m(t) \quad \text{where, } \omega_{mn} = \frac{E_m - E_n}{\hbar}$$

$$\frac{1}{i\hbar} \sum_n c_n(t) V_{mn}(t) e^{i\omega_{mn} t} = \dot{c}_m(t)$$

6.3.1 Two-level system

- Since there are only two states, we can simply write out the explicit expressions for the coefficient derivatives:

$$\begin{aligned}\dot{c}_1 &= \frac{1}{i\hbar} c_1 V_{11} + \frac{1}{i\hbar} c_2 V_{12} e^{i\omega_{12} t} \\ \dot{c}_2 &= \frac{1}{i\hbar} c_1 V_{21} e^{i\omega_{21} t} + \frac{1}{i\hbar} c_2 V_{22}\end{aligned}$$

where it is understood that the coefficients and \hat{V} depend on time.

- Often the time dependent piece is an odd function, so the diagonal terms are zero. We will assume this to be the case here.

$$\begin{aligned}\dot{c}_1 &= \frac{1}{i\hbar} c_2 V_{12} e^{i\omega_{12} t} \\ \dot{c}_2 &= \frac{1}{i\hbar} c_1 V_{21} e^{i\omega_{21} t}\end{aligned}$$

- Initial Conditions:** Let's consider a situation in which a system starts out completely in state 1, $c_1(0) = 1$, and at $t = 0$, a *constant* potential is turned on until it is turned off at $t = T$. Thus, in this example, the time-dependent potential is a step function.

- Start by getting an equation in terms of derivatives of only one variable.

$$c_1 = \frac{i\hbar}{V_{21}} e^{-i\omega_{21} t} \dot{c}_2$$

- Now differentiate the \dot{c}_2 equation again:

$$\begin{aligned}\ddot{c}_2 &= \frac{V_{21}}{i\hbar} e^{i\omega_{21} t} \dot{c}_1 + \frac{V_{21}}{i\hbar} (i\omega_{21}) e^{i\omega_{21} t} c_1 \\ &= \frac{V_{21}}{i\hbar} e^{i\omega_{21} t} \left(\frac{1}{i\hbar} c_2 V_{12} e^{i\omega_{12} t} \right) + \frac{V_{21}}{i\hbar} (i\omega_{21}) e^{i\omega_{21} t} \left(\frac{i\hbar}{V_{21}} e^{-i\omega_{21} t} \dot{c}_2 \right) \quad \text{sub} \\ &= - \left| \frac{V_{21}}{\hbar} \right|^2 c_2 + i\omega_{21} \dot{c}_2\end{aligned}$$

- Second-order differential equation:

$$A\ddot{c}_2 + B\dot{c}_2 + Cc_2 = 0$$

where,

$$\begin{aligned} A &= 1 \\ B &= -i\omega_{21} \\ C &= \left| \frac{V_{21}}{\hbar} \right|^2 \end{aligned}$$

- Try a solution of the form: $c_2(t) = ke^{rt}$

$$\begin{aligned} ke^{rt}r^2 + ke^{rt}rB + ke^{rt}C &= 0 \\ ke^{rt} \left(r^2 + Br + C \right) &= 0 \end{aligned} \quad \text{quadratic equation in } r$$

using the quadratic equation,

$$\begin{aligned} r &= -\frac{B}{2} \pm \frac{1}{2}\sqrt{B^2 - 4C} \\ &= \frac{i\omega_{21}}{2} \pm \frac{1}{2}\sqrt{-\omega_{21}^2 - 4\left|\frac{V_{21}}{\hbar}\right|^2} \\ &= \frac{i\omega_{21}}{2} \pm i\Omega \quad \Omega = \frac{1}{2}\sqrt{\omega_{21}^2 + \frac{4}{\hbar^2}|V_{21}|^2} \end{aligned}$$

so,

$$c_2(t) = e^{\frac{i\omega_{21}}{2}t} \left[k_1 e^{i\Omega t} + k_2 e^{-i\Omega t} \right]$$

- Use initial conditions, $c_2(t = 0) = 0$:

$$k_1 = -k_2$$

so,

$$c_2(t) = 2ike^{\frac{i\omega_{21}}{2}t} \sin \Omega t$$

- Use above equation to solve for $c_1(t)$:

$$\begin{aligned} c_1 &= \frac{i\hbar}{V_{21}} e^{-i\omega_{21}t} \dot{c}_2 \\ &= \frac{i\hbar}{V_{21}} e^{-i\omega_{21}t} \left[2ike^{\frac{i\omega_{21}}{2}t} \sin \Omega t \left(\frac{i\omega_{21}}{2} \right) + 2ike^{\frac{i\omega_{21}}{2}t} \cos \Omega t \Omega \right] \\ &= \frac{k\hbar}{V_{21}} e^{\frac{-i\omega_{21}}{2}t} [-i\omega_{21} \sin \Omega t - 2\Omega \cos \Omega t] \end{aligned}$$

- Require normalization at boundary condition $\int dx \Psi(0)^* \Psi(0) = 1$

$$\begin{aligned}\langle \Psi(0) | \Psi(0) \rangle &= 1 \\ &= c_1(0)^* c_1(0) \\ &= \left(\frac{-2k\hbar\Omega}{V_{21}} \right)^2 \\ k &= \frac{V_{21}}{2\hbar\Omega}\end{aligned}$$

- Now we can write down the full expressions,

$$\begin{aligned}c_2(t) &= i \frac{V_{21}}{\hbar\Omega} e^{\frac{i\omega_{21}}{2}t} \sin \Omega t \\c_1(t) &= -e^{\frac{-i\omega_{21}}{2}t} \left[\frac{i\omega_{21}}{2\Omega} \sin \Omega t + \cos \Omega t \right]\end{aligned}$$

- This is the exact solution, given the particular constant form of the time dependent operator $\hat{V}(t) = V$, and initial conditions (the state starts in level 1)
- How does state occupation evolve in time? → Rabi formula

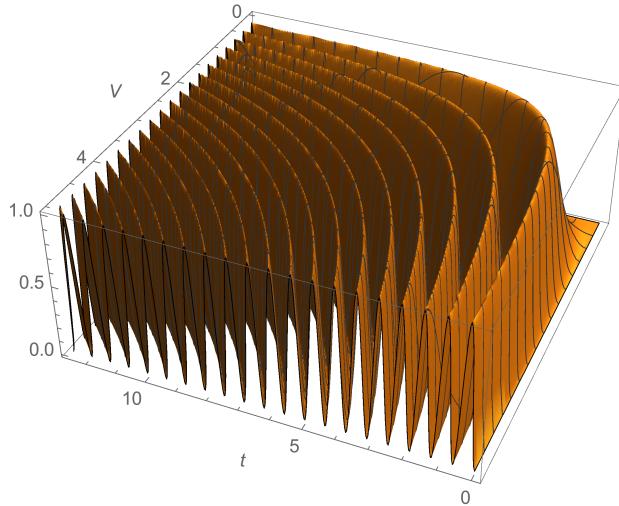
- Probability of being in level 2:

$$\begin{aligned}P_2(t) &= \frac{|V|^2}{\hbar^2\Omega^2} \sin^2(\Omega t) \\ &= \frac{4|V|^2}{\hbar^2\omega_{21}^2 + 4|V|^2} \sin^2 \left(\sqrt{\frac{\omega_{21}^2}{4} + \frac{|V|^2}{\hbar^2}} t \right)\end{aligned}$$

- **Case 1:** Degenerate levels, $\omega_{21} = 0$

$$P_2(t) = \sin^2 \left(\frac{|V|}{\hbar} t \right)$$

here, the system goes back and forth between the states, with a frequency which depends on the strength of the perturbation



- **Case 2:** Big Gap/Small perturbation, $\hbar^2 \omega_{21}^2 \gg 4|V|^2$

$$P_2(t) \approx \left(\frac{2|V|}{\hbar \omega_{21}} \right)^2 \sin^2 \left(\frac{\omega_{21}}{2} t \right)$$

here, the system goes partially back and forth between the states, with a frequency which depends on the gap between the states. Full population transfer does not occur, but depends on the strength of the perturbation.

6.3.2 Many-level systems

- We have already discussed the general strategy for solving the TDSE: expand the TDSE solutions $|\Psi(t)\rangle$ as a linear combination of stationary states, $|\Psi_n^{(0)}(t)\rangle$

$$\begin{aligned} |\Psi(t)\rangle &= \sum_n c_n |\Psi_n^{(0)}(t)\rangle \\ &= \sum_n c_n |n\rangle e^{-iE_n t/\hbar} \end{aligned}$$

- We then derived the general expression for the derivative of the coefficients

$$\dot{c}_m(t) = \frac{1}{i\hbar} \sum_n c_n(t) V_{mn}(t) e^{i\omega_{mn} t}$$

- To solve this we will make some assumptions, and then some approximations.
 1. Small perturbation: $\hat{V}(t) \ll \omega_{nk}$
 2. System starts in ground state: $c_0(t=0) = 1$
- Since the perturbation is small, in the time immediately following t_0 , the system will largely remain in the ground state, suggesting a perturbative expansion about t_0

$$\begin{aligned} \hat{H} &= \hat{H}^{(0)} + \lambda \hat{V}(t) \\ c_k(t) &= c_k(0) + \lambda c_k^{(1)}(t) + \lambda^2 c_k^{(2)}(t) + \dots & c_k^{(0)}(t) &= c_k(0) \end{aligned}$$

- Substitute this expansion into the equation above:

$$\dot{c}_m(t) = \frac{1}{i\hbar} \sum_n c_n(t) V_{mn}(t) e^{i\omega_{mn} t}$$

$$\frac{d}{dt} \left(c_m(0) + \lambda c_m^{(1)}(t) + \dots \right) = \frac{1}{i\hbar} \sum_n \lambda V_{mn}^{(1)}(t) e^{i\omega_{mn} t} \left(c_n(0) + \lambda c_n^{(1)}(t) + \dots \right)$$

- Collect orders:

$$\frac{d}{dt} c_m(0) = 0 \quad : \lambda^0$$

$$\frac{d}{dt} c_m^{(1)}(t) = \frac{1}{i\hbar} \sum_n V_{mn}^{(1)}(t) e^{i\omega_{mn} t} c_n(0) \quad : \lambda^1$$

However, at $t = 0$, only ground state is occupied $c_0(0) = 1$, so,

$$\frac{d}{dt} c_m^{(1)}(t) = \frac{1}{i\hbar} V_{m0}^{(1)}(t) e^{i\omega_{m0} t}$$

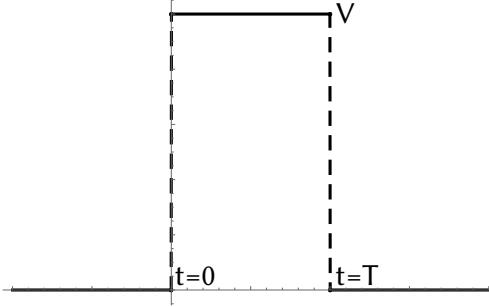
- We can directly integrate this to get the coefficients,

$$c_m^{(1)}(t) = c_m(0) + \frac{1}{i\hbar} \int_{t'=0}^{t'=t} V_{m0}^{(1)}(t') e^{i\omega_{m0} t'} dt'$$

Notice that this is simply the Fourier Transform of the perturbation!

- In order to proceed, we must know something about the functional form of the perturbation so as to integrate it!
- **Case 1:** Static potential

- If a constant perturbation is abruptly switched on at $t = 0$, and turned off at $t = T$ (like we did with the 2-level system),



- For this potential we can break up the integral,

$$c_k^{(1)}(t) = c_k^{(0)} - \frac{i}{\hbar} \left[\int_0^T dt' + \int_T^t dt' \right] V_{k0}(t') e^{-i\omega_{k0} t'}$$

- from this it's clear that after the potential is turned off, the coefficient remains unchanged from $c_k^{(1)}(T)$, so we will just focus on what happens leading up to that point, $t < T$.

$$\begin{aligned} c_k^{(1)}(t) &= c_k^{(0)} - \frac{iV_{k0}}{\hbar} \int_0^t dt' e^{-i\omega_{k0}t'} \\ &= \delta_{0k} + \frac{V_{k0}}{\hbar} \frac{1}{\omega_{k0}} (e^{-i\omega_{k0}t} - 1) \end{aligned}$$

- Let's look at the probability for the system to be in an excited state, i.e., $k \neq 0$

$$\begin{aligned} P_k^{(1)}(t) &= \frac{V_{k0}^2}{\hbar^2 \omega_{k0}^2} (e^{i\omega_{k0}t} - 1)(e^{-i\omega_{k0}t} - 1) \\ &= \frac{V_{k0}^2}{\hbar^2 \omega_{k0}^2} (1 - e^{i\omega_{k0}t} - e^{-i\omega_{k0}t} + 1) \\ &= \frac{V_{k0}^2}{\hbar^2 \omega_{k0}^2} (2 - 2 \cos(\omega_{k0}t)) && \text{Euler's formula} \\ &= \frac{2V_{k0}^2}{\hbar^2 \omega_{k0}^2} \left(1 - \left[1 - 2 \sin^2\left(\frac{\omega_{k0}}{2}t\right)\right]\right) && \text{double angle} \\ &= \frac{4V_{k0}^2}{\hbar^2 \omega_{k0}^2} \sin^2\left(\frac{\omega_{k0}}{2}t\right) \end{aligned}$$

- This is exactly what we got for the 2-level system, when we had a big gap!
- Each excited state then accrues population in an identical (to first order) way as a 2-level system

Start of Lecture 18

- **Case 2:** Oscillating potential

- now let's consider the case in which the time dependent part of the hamiltonian is an oscillating electric field,

$$\hat{H} = \hat{H}^{(0)} + 2V \cos(\omega t) \quad \text{where, } \omega = 2\pi\nu$$

- Remembering our equation for expressing the TDSE in the basis of stationary states, we can substi-

tute the above potential:

$$\begin{aligned}
 c_m^{(1)}(t) &= c_m(0) + \frac{1}{i\hbar} \int_{t'=0}^{t'=t} V_{m0}^{(1)}(t') e^{i\omega_{m0} t'} dt' \\
 &= \frac{2V_{m0}}{i\hbar} \int_{t'=0}^{t'=t} \cos(\omega t') e^{i\omega_{m0} t'} dt' \\
 &= \frac{V_{m0}}{i\hbar} \int_{t'=0}^{t'=t} (e^{i\omega t'} + e^{-i\omega t'}) e^{i\omega_{m0} t'} dt' && \text{Euler} \\
 &= \frac{V_{m0}}{i\hbar} \int_{t'=0}^{t'=t} (e^{i(\omega_{m0}+\omega)t'} + e^{i(\omega_{m0}-\omega)t'}) dt' \\
 &= \frac{V_{m0}}{i\hbar} \int_{t'=0}^{t'=t} (e^{i\omega_+ t'} + e^{i\omega_- t'}) dt' && \omega_{\pm} = \omega_{m0} \pm \omega \\
 &= -\frac{V_{m0}}{\hbar\omega_+} (e^{i\omega_+ t} - 1) - \frac{V_{m0}}{\hbar\omega_-} (e^{i\omega_- t} - 1)
 \end{aligned}$$

- Considering the typical case where our system starts in a low energy state and has the possibility to transition to higher energy states: $\omega_{m0} = \frac{E_m - E_0}{\hbar} > 0$, we can notice that if we add the frequency of the oscillating potential ω_+ , then this value only gets larger.
- Thus, in the perturbative regime, $\frac{V_{m0}}{\omega_{m0}} \ll 1$, the first term is small compared to the second term, and becomes vanishingly small when ω approaches ω_{m0} .

$$c_m^{(1)}(t) \approx -\frac{V_{m0}}{\hbar\omega_-} (e^{i\omega_- t} - 1)$$

- The probability of making a transition to state m is,

$$\begin{aligned}
 P_m^{(1)}(t) &= \frac{|V_{m0}|^2}{\hbar^2\omega_-^2} (1 - e^{-i\omega_- t} - e^{i\omega_- t} + 1) \\
 &= \frac{|V_{m0}|^2}{\hbar^2\omega_-^2} (2 - 2\cos(\omega_- t)) \\
 &= \frac{|V_{m0}|^2}{\hbar^2\omega_-^2} \left(2 - 2(1 - 2\sin^2\left(\frac{\omega_- t}{2}\right)) \right) && \text{double angle} \\
 &= \frac{4|V_{m0}|^2}{\hbar^2\omega_-^2} \sin^2\left(\frac{\omega_- t}{2}\right)
 \end{aligned}$$

- If the frequency of the oscillating perturbation is zero, $\omega = 0$, then the results are identical to the constant field results (as one should expect).
- One can interpret this result as if the oscillating field changes the energy gaps of the system, providing an “effective” energy gap.

- If $\omega \rightarrow \omega_{m0}$, then the “effective energy gap” drops to zero, and the system should behave as a degenerate system, which can transfer all of its population.

$$\begin{aligned}
 \lim_{\omega \rightarrow \omega_{m0}} P_m^{(1)}(t) &= \lim_{\omega \rightarrow \omega_{m0}} \frac{4|V_{m0}|^2}{\hbar^2 \omega_-^2} \sin^2 \left(\frac{\omega_- t}{2} \right) \\
 &= \lim_{\omega \rightarrow \omega_{m0}} \frac{4|V_{m0}|^2}{\hbar^2 \omega_-^2} \left(\frac{\omega_- t}{2} - \frac{\omega_-^3 t^3}{2^3 \cdot 3!} + \frac{\omega_-^5 t^5}{2^5 \cdot 5!} - \dots \right)^2 \quad \text{Taylor series} \\
 &= \lim_{\omega \rightarrow \omega_{m0}} \frac{4|V_{m0}|^2}{\hbar^2} \left(\frac{t}{2} - \frac{\omega_-^2 t^3}{2^3 \cdot 3!} + \frac{\omega_-^4 t^5}{2^5 \cdot 5!} - \dots \right)^2 \\
 &= \frac{|V_{m0}|^2}{\hbar^2} t^2
 \end{aligned}$$

$$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \dots$$

6.3.3 Transitions to several possible states

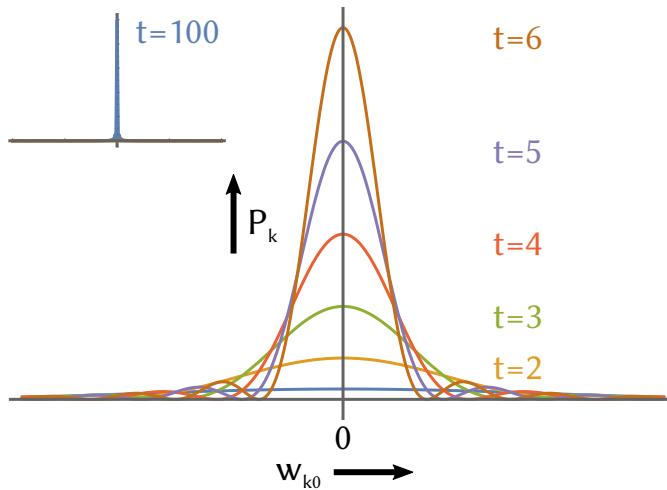
- Assuming we can truncate after first order in the perturbation, the transition probability is given as:

$$P_m(t) = \frac{4|V_{m0}|^2}{\hbar^2 \omega_{k0}^2} \sin^2 \left(\frac{\omega_{k0} t}{2} \right) \quad \omega_{k0} \text{ either bare or shifted energy gap}$$

which (if V_{k0} is slowly varying with k) is essentially just a squared “sinc” function.

$$P_m(t) = \frac{|V_{m0}|^2}{\hbar^2} \operatorname{sinc}^2 \left(\frac{\omega_{k0} t}{2} \right) \quad \operatorname{sinc}(x) = \sin(x)/x$$

- It is easily seen that when the transition frequency $\omega_{k0} = 0$ (or when $\omega - \omega_{k0} = 0$ in an oscillating field) the probability of transitioning to state k increases quadratically, also seen from the limit above. This results in a highly peaked function, which tells us that the only state to which a transition is likely to occur is a transition where $\omega_{k0} = 0$ (and $V_{m0} \neq 0$).



- That this can (unphysically) exceed unit probability is a consequence of first order perturbation theory.

6.3.4 Fermi's Golden Rule

- Here, we will consider what happens if a system has the opportunity to transition from initial state $|i\rangle$ (not necessarily the ground state) to a continuum of energy states, such that we must introduce a density of states, $\rho(E_k)$, (i.e., the number of states inside the region $E_k + \delta k$).

$$\rho(E_k) = \frac{dk}{dE_k} \implies \rho(E_k)dE_k = dk \quad (189)$$

- Examples:

- Electron transfer kinetics: Marcus theory
- Förster energy transfer
- Internal conversion/non-radiative decay/intersystem crossing
- β -decay of a neutron
- many more!

- Start with a few assumptions:

- assume “long” time compared to energy gaps: $t \gg \frac{2\pi}{\omega_{k0}}$
- assume V_{k0} is slowly varying with k : $\frac{dV_{k0}}{dk} \ll 1$
- assume $\rho(E_k)$ is slowly varying with k : $\frac{d\rho(E_k)}{dk} \ll 1$

- Each possible transition has a probability $P_k(t)$, but since there are multiple states with a given energy E_k (such that $\omega_{k0} = 0$), then the total probability is a sum over all the total possible states with energy

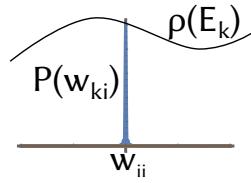
E_k .

$$P(t) = \sum_k P_k(t) \quad \text{add up all transitions} \quad (190)$$

$$\Rightarrow \int dk P_k(t) \quad \text{continuous} \quad (191)$$

$$= \int dE_k \rho(E_k) P_k(t) \quad \text{substitute for } dk \quad (192)$$

Substitute in for $P_k(t)$, and recognize that since the sinc function is sharply peaked around the initial state i , that only the behavior of both the density of states and the matrix element around $k = i$ is needed. And since we have assumed these are slowly varying quantities, then they are effectively constant in the region around i “plucked out” by the sinc function.



$$P(t) = \int dE_k \rho(E_k) \frac{4|V_{mi}|^2}{\hbar^2 \omega_{ki}^2} \sin^2 \left(\frac{\omega_{ki}t}{2} \right) \quad (193)$$

$$= \frac{|V_i|^2 \rho(E_i)}{\hbar^2} \int dE_k \frac{\sin^2 \left(\frac{\omega_{ki}t}{2} \right)}{\left(\frac{\omega_{ki}}{2} \right)^2} \quad (194)$$

This integral is easily evaluated, noting that $\int_{-\infty}^{\infty} dx \operatorname{sinc}(x)^2 = \pi$. Let

$$x = \frac{\omega_{ki}t}{2} = \frac{(E_k - E_i)t}{2\hbar} \quad (195)$$

$$dx = \frac{d\omega_{ki}t}{2} = \frac{dE_k t}{2\hbar} \quad (196)$$

$$\Rightarrow dE_k = \frac{2\hbar}{t} dx \quad (197)$$

Inserting this into the above equation yields:

$$\int_{-\infty}^{\infty} dx \operatorname{sinc}(x)^2 = \int_{-\infty}^{\infty} \frac{dE_k t}{2\hbar} \frac{\sin^2 \left(\frac{\omega_{ki}t}{2} \right)}{\left(\frac{\omega_{ki}t}{2} \right)^2} \quad (198)$$

$$= \pi \quad (199)$$

We can rearrange this to see that:

$$\int dE_k \frac{\sin^2 \left(\frac{\omega_{ki}t}{2} \right)}{\left(\frac{\omega_{ki}}{2} \right)^2} = 2\pi\hbar t \quad (200)$$

such that the probability is linear in time:

$$P(t) = \frac{2\pi|V_i|^2\rho(E_i)}{\hbar}t \quad (201)$$

- The transition rate, is the change in the probability with respect to time:

$$k(t) = \frac{dP(t)}{dt} = \frac{2\pi|V_i|^2\rho(E_i)}{\hbar} \quad (202)$$

- Thus, the decay rate (i.e., the rate of population loss from state $|i\rangle$ to a continuum of states) is independent of time, and is completely determined by a characteristic coupling matrix element, and the continuum's density of states near the initial state's energy. This is known as Fermi's Golden Rule !

Start of Lecture 19

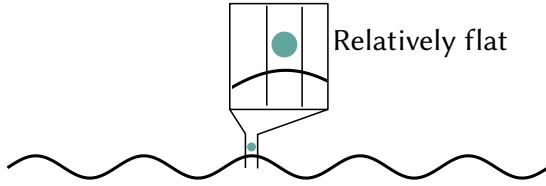
7 Many-electron systems

7.1 Hydrogen atom spectrum

7.1.1 Selection rules

- What happens when you hit a Hydrogen atom with a photon?
- An electromagnetic wave can be represented approximately as:

$$\vec{E} = 2\vec{E}_0 \cos \omega t$$



- The interaction of an atom with this field gives the following interaction potential

$$V^{(1)}(t) = -2\hat{\mu} \cdot \vec{E}_0 \cos \omega t,$$

where $\vec{\mu}$ is the electric dipole moment operator:

$$\begin{aligned}\hat{\mu} &= \hat{\mu}_x \vec{e}_x + \hat{\mu}_y \vec{e}_y + \hat{\mu}_z \vec{e}_z \\ &= -e (\hat{X} \vec{e}_x + \hat{Y} \vec{e}_y + \hat{Z} \vec{e}_z) \\ &= -e \hat{R}\end{aligned}$$

- Thus, we know that the transition from $|i\rangle$ to $|f\rangle$ occurs with the following probability (to first order):

$$\begin{aligned}P_{if}^{(1)}(t) &= \frac{|V_{if}|^2}{\hbar^2} \left(\frac{\sin(\frac{\omega}{2}t)}{\frac{\omega}{2}} \right)^2 \\ &= \frac{|\langle i | \hat{\mu} | f \rangle|^2 \cdot \vec{E}_0^2}{\hbar^2} \left(\frac{\sin(\frac{\omega}{2}t)}{\frac{\omega}{2}} \right)^2 \\ &= \frac{e^2 |\langle i | \hat{R} | f \rangle|^2 \cdot \vec{E}_0^2}{\hbar^2} \left(\frac{\sin(\frac{\omega}{2}t)}{\frac{\omega}{2}} \right)^2 \\ &\propto |\langle i | \hat{\mu} | f \rangle|^2\end{aligned}$$

- Thus, $\langle i | \hat{\mu} | f \rangle \neq 0$ is required to observe a transition
- **Laporte Selection rule:** Required $(-1)^{l_i} \neq (-1)^{l_f}$, change in parity (for systems with inversion symmetry, u to g transitions allowed)

- $\Delta l = \pm 1$
Symmetry or conservation of the photon's angular momentum
- $\Delta m_l = 0, \pm 1$
Suppose light is plane-polarized (z):

- $\langle i | \hat{\mu} | f \rangle \Rightarrow \langle i | \hat{\mu}_z | f \rangle$
- and, $\hat{\mu}_z = -er \cos \theta$, so

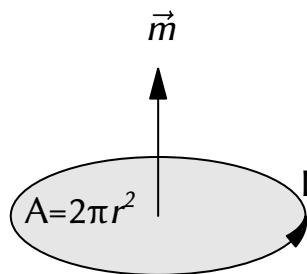
$$\langle f | \hat{\mu}_z | i \rangle \propto \int_0^{2\pi} e^{-im_{lf}\phi} e^{im_i\phi} d\phi = \int e^{i\Delta m_l \phi} d\phi$$

which equals 0, unless $\Delta m_l = 0$

- Considering x and y polarized light leads to $\Delta m_l = \pm 1$ cases

7.1.2 Spin Orbit Coupling

- Charged particle + angular momentum = magnetic moment



- 2 sources of angular momentum: orbital and spin
- Orbital angular momentum has a classical analogue, so we consider this first. Classically, magnetic momentum is given by:

$$\vec{m} = \frac{q}{2} \vec{r} \times \vec{v}$$

But remember that angular momentum looks very similar,

$$\begin{aligned} \vec{l} &= \vec{r} \times \vec{p} \\ &= m \vec{r} \times \vec{v} \end{aligned}$$

so,

$$\begin{aligned} \vec{m} &= \frac{q}{2m} \vec{l} \\ &= \gamma \vec{l} \end{aligned}$$

- The magnetic moment and the angular momentum are proportional. For a single electron moving about a fixed radius (in an orbital), the proportionality constant, γ_e , is the magnetogyric ratio of the electron:

$$\gamma_e = \frac{-e}{2m_e}$$

- We can multiply that by \hbar to get the Bohr magneton, μ_B

$$\mu_B = -\gamma\hbar$$

such that

$$m_z = -\mu_B m_l$$

m_l is quantum number

- What about spin angular momentum? No classical analogue. Need to solve the relativistic Dirac equation.

Spin magnetic moment $\vec{m} \propto \vec{s}$

$$M_z \propto m_s$$

- we might think $M_z = \gamma e \hbar m_s$
- ~~Dirac~~ Relativistic consideration show us that otherwise
- $M_z = \frac{\gamma}{2} e \hbar m_s$
- QED further says

$$M_z = 2.0028 \gamma e \hbar m_s$$

γ_e

$$M_z = g_e \gamma e \hbar m_s = -g_e \mu_B m_s$$



$l: \uparrow, s: \uparrow$

- The interaction of these magnetic moments has an energetic consequence
- Dirac Equation yields

$$\hat{H}_{so} = f(r) \hat{l} \cdot \hat{s}$$

- where $f(r) = -\frac{e}{2m_e^2 r c^2} \frac{\partial \phi}{\partial r}$ electric potential

$$\hat{\vec{l}} \cdot \hat{\vec{S}} = (\hat{l}_x + \hat{l}_y + \hat{l}_z)(s_x + s_y + s_z)$$

$$\hat{j} = \hat{l} + \hat{s}$$

$$\hat{j}^2 = \hat{l}^2 + \hat{s}^2 + 2\hat{l} \cdot \hat{s}$$

$$\hat{H}_{so} = \frac{e}{2} (j^2 - l^2 - s^2)$$

State of Hydrogen, $|n, l, m_l, s, m_s\rangle \rightarrow |n, l, s, j, m_j\rangle$

$$E_{so} = \langle n, l, s, j, m_j | H_{so} | n, l, s, j, m_j \rangle$$

$$= \frac{hc}{\hbar^2} \zeta_{nl} \left(2(j+1) - l(l+1) - s(s+1) \right) \hbar^2$$

comes from radial wavefunction

$$\begin{aligned} \frac{1}{2}P_{\frac{3}{2}} & \quad P' \quad \left| 1, 1, \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right\rangle \quad \text{Max} \quad j = \frac{3}{2} \quad m_j = \frac{3}{2} \quad \text{so} \quad j = \frac{3}{2} \\ & \quad \downarrow \quad \left| 1, 1, \frac{1}{2}, \frac{1}{2}, \frac{3}{2} \right\rangle \quad \text{or} \quad \left| 1, 1, \frac{1}{2}, \frac{3}{2}, \frac{1}{2} \right\rangle \quad \text{or} \quad \left| 1, 1, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right\rangle \end{aligned}$$

$$\frac{1}{2}P_{\frac{3}{2}}: E_{so} = hc \zeta_{nl} \left(\frac{15}{4} - \frac{4}{2} - \frac{3}{4} \right) = hc \zeta_{nl} \left(\dots \right)$$

$$\frac{1}{2}P_{\frac{1}{2}}: E_{so} = hc \zeta_{nl} \left(\frac{3}{4} - \frac{4}{2} - \frac{3}{4} \right) = -2hc \zeta_{nl}$$

Start of Lecture 20

7.2 Helium Atom

- Simplest example of many-electron system: He atom
- No analytic solution, due to electron-electron repulsion

$$\hat{H} = \frac{-\hbar^2}{2m_e} (\Delta_1^2 + \Delta_2^2) - \frac{2e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}}$$

- Simplify this Hamiltonian - convert to **atomic units** (au)

- Start with Hydrogen atom Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_e} \Delta^2 - \frac{e^2}{4\pi\epsilon r} \right) \psi(r) = E\psi(r)$$

- Let us scale the coordinates such that $r = \lambda r'$

$$\left(-\frac{\hbar^2}{2m_e \lambda^2} \Delta'^2 - \frac{e^2}{4\pi\epsilon \lambda r'} \right) \psi(r') = E\psi(r')$$

- We'd like to be able to factor out the constants. We can only do that if:

$$\frac{\hbar^2}{m_e \lambda^2} = \frac{e^2}{4\pi\epsilon_0 \lambda} = k$$

thus,

$$\lambda = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

- Consider the units of λ : $(F/m)(J s)^2/(C^2 kg) = (C^2/mJ)(J^2 s^2)/(C^2 kg) = (1/m)(Js^2)/(kg) = (1/m)(kg m^2 s^{-2} s^2)/(kg) = (m)$ distance
- λ is a standard distance called a **Bohr radius**
- Consider k

$$k = m_e \left(\frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 \quad \text{units of energy}$$

- k is a unit of energy called a **Hartree**
- We can now rewrite the Schrödinger equation in these atomic units:

$$\left(-\frac{1}{2} \Delta'^2 - \frac{1}{r'} \right) \psi(r') = \frac{E}{k} \psi(r')$$

- and now the Helium atom Hamiltonian is,

$$\hat{H} = \frac{-1}{2} (\Delta_1^2 + \Delta_2^2) - 2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} \quad \text{dropping the '}$$

7.2.1 Slater Determinant

- Although, we have solved for the exact Hydrogen orbitals, the solutions to a Helium atom, is not possible. Perhaps we can use the Hydrogen atom solutions to help our efforts at solving the Helium atom.
- In this direction, if the interelectronic repulsion term were not present, we would have a separable equation, such that a product of 1-particle solutions (hydrogenic “orbitals”) would also be a solution:

$$(\hat{H}_1 + \hat{H}_2) \psi_1(r_1)\psi_2(r_2) = (E_1 + E_2) \psi_1(r_1)\psi_2(r_2)$$

- Remember, the only thing we get from the hydrogen atom is n, l, m_l ; spin quantum numbers can only be rigorously added after solving the Dirac equation.
- Let us now refer to these purely spatial functions (defined by n, l, m_l) as **spatial orbitals**, $\psi(r)$
- Defining functions which also involve spin coordinates, we further define **spin orbitals**, $\chi(x) = \psi(r)\sigma(\omega)$, where $\sigma(\omega)$ could either be α or β spin
- An approximate many-electron wavefunction, which is obtained by taking a product of spin orbitals is called a **Hartree product**
- Unfortunately, a Hartree product does not satisfy one of the fundamental requirements of a Fermionic wavefunction:

Definition: Pauli exclusion principle

The total wavefunction for two Fermions is antisymmetric with respect to exchange of any two particles.

$$\psi(r_1, r_2) = -\psi(r_2, r_1)$$

Thus if we exchange the electron indices in a Hartree product:

$$\mathcal{P}(1,2)\psi_1(r_1)\psi_2(r_2) = \psi_1(r_2)\psi_2(r_1) \neq -\psi_1(r_1)\psi_2(r_2)$$

we don't get the same wavefunction back plus a sign.

- Put in a different way, “No two electrons can have the same *quantum address*” (set of quantum numbers, n, l, m_l, s, m_s)
- A spatial orbital can have occupations, 0, 1, or 2, while a spin orbital can only have 0 or 1.
- Although a single Hartree product does not satisfy the Pauli exclusion principle, a linear combination can:

$$\begin{aligned} \Psi(r_1, r_2) &= \chi_1(r_1)\chi_2(r_2) - \chi_2(r_1)\chi_1(r_2) \\ \mathcal{P}(1,2)\Psi(r_1, r_2) &= \chi_1(r_2)\chi_2(r_1) - \chi_2(r_2)\chi_1(r_1) \\ &= \Psi(r_2, r_1) = -\Psi(r_1, r_2) \end{aligned}$$

- Notice that this linear combination can be written as the determinant of a matrix:

$$\det \begin{Bmatrix} \chi_1(r_1) & \chi_1(r_2) \\ \chi_2(r_1) & \chi_2(r_2) \end{Bmatrix} = \chi_1(r_1)\chi_2(r_2) - \chi_2(r_1)\chi_1(r_2)$$

- This can be further generalized to N -electron systems. The normalized form is called a **Slater determinant wavefunction**.

$$\Psi^{SD}(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} \det \begin{Bmatrix} \chi_1(r_1) & \chi_1(r_2) & \cdots & \chi_1(r_N) \\ \chi_2(r_1) & \chi_2(r_2) & \cdots & \chi_2(r_N) \\ \vdots & & & \\ \chi_N(r_1) & \chi_N(r_2) & \cdots & \chi_N(r_N) \end{Bmatrix}$$

- The determinantal form of the wavefunction, ensure antisymmetry and single occupation of spin orbitals. For instance, suppose we tried to put two electrons inside of a single spin orbital:

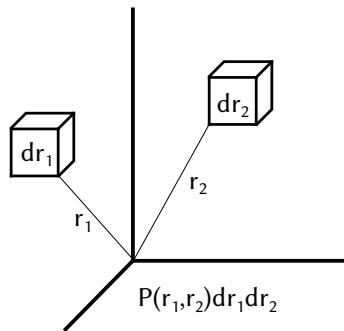
$$\Psi^{SD}(r_1, r_2) = \frac{1}{\sqrt{2}} (\chi_1(r_1)\chi_1(r_2) - \chi_1(r_2)\chi_1(r_1)) = 0$$

This is also a general property of a determinant of a matrix: if two columns are the same the determinant is zero, and if you swap two columns, the determinant picks up a negative sign

7.2.2 Statistical Correlation

- The Slater determinant introduces correlated motions of electrons of same spin

$$\begin{aligned} 1 &= \int d\mathbf{x}_1 d\mathbf{x}_2 |\Psi(\mathbf{x}_1, \mathbf{x}_2)|^2 \\ &= \int dr_1 dr_2 d\omega_1 d\omega_2 |\Psi(\mathbf{x}_1, \mathbf{x}_2)|^2 \\ &= \int dr_1 dr_2 P(r_1, r_2) \end{aligned}$$



$$\begin{aligned} P(r_1, r_2) &= \frac{1}{2} \int d\omega_1 d\omega_2 |\psi_1(r_1)\psi_2(r_2)\sigma_1(\omega_1)\sigma_2(\omega_2) - \psi_1(r_2)\psi_2(r_1)\sigma_1(\omega_2)\sigma_2(\omega_1)|^2 \\ &= \frac{1}{2} \int d\omega_1 d\omega_2 [| \psi_1(r_1) |^2 | \psi_2(r_2) |^2 + | \psi_1(r_2) |^2 | \psi_2(r_1) |^2 \\ &\quad - \psi_1^*(r_1)\psi_2(r_1) \cdot \psi_2^*(r_2)\psi_1(r_2) \cdot \sigma_1^*(\omega_1)\sigma_2(\omega_1) \cdot \sigma_2^*(\omega_2)\sigma_1(\omega_2) - c.c.] \end{aligned}$$

- **CASE 1:** The spins are not the same

- i.e., $\sigma_1 = \alpha$ and $\sigma_2 = \beta$ then,

$$P(r_1, r_2) = \frac{1}{2} (| \psi_1(r_1) |^2 | \psi_2(r_2) |^2 + | \psi_1(r_2) |^2 | \psi_2(r_1) |^2)$$

- if $\psi_1 = \psi_2$,

$$P(r_1, r_2) = | \psi_1(r_1) |^2 | \psi_1(r_2) |^2$$

- the probability density becomes the product of the densities: uncorrelated
- They can exist in the same location $P(r_1, r_1) \neq 0$

- **CASE 2:** The spins are the same

- i.e., $\sigma_1 = \alpha$ and $\sigma_2 = \alpha$ then,

$$\begin{aligned} P(r_1, r_2) &= \frac{1}{2} (| \psi_1(r_1) |^2 | \psi_2(r_2) |^2 + | \psi_1(r_2) |^2 | \psi_2(r_1) |^2 \\ &\quad - \psi_1^*(r_1)\psi_2(r_1) \cdot \psi_2^*(r_2)\psi_1(r_2) - \psi_1^*(r_2)\psi_2(r_2) \cdot \psi_2^*(r_1)\psi_1(r_1)) \end{aligned}$$

- Particles are correlated, **Fermi hole**

$$\begin{aligned} P(r_1, r_1) &= \frac{1}{2} (| \psi_1(r_1) |^2 | \psi_2(r_1) |^2 + | \psi_1(r_1) |^2 | \psi_2(r_1) |^2 \\ &\quad - \psi_1^*(r_1)\psi_2(r_1) \cdot \psi_2^*(r_1)\psi_1(r_1) - \psi_1^*(r_1)\psi_2(r_1) \cdot \psi_2^*(r_1)\psi_1(r_1)) \\ &= 0 \end{aligned}$$

7.3 Hartree-Fock

7.3.1 Energy of a Slater Determinant

- The Hamiltonian can be broken up into 1 and 2 electron terms
- For simplicity, let's consider again, the Helium Hamiltonian

$$\begin{aligned} \hat{H} &= \frac{-1}{2} (\Delta_1^2 + \Delta_2^2) - 2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} \\ &= O_1 + O_2 \\ &= \hat{h}(x_1) + \hat{h}(x_2) + \hat{v}(x_1, x_2) \end{aligned}$$

- Expectation value of a 1-electron operator with a Slater Determinant wavefunction

$$\begin{aligned}
 \langle \Psi^{SD} | \hat{h}(x_1) | \Psi^{SD} \rangle &= \frac{1}{2} \int dx_1 dx_2 [\chi_1(x_1)\chi_2(x_2) - \chi_1(x_2)\chi_2(x_1)]^* \\
 &\quad \hat{h}(x_1) [\chi_1(x_1)\chi_2(x_2) - \chi_1(x_2)\chi_2(x_1)] \\
 &= \frac{1}{2} \int dx_1 (\chi_1(x_1)^* \hat{h}(x_1) \chi_1(x_1) + \chi_2(x_1)^* \hat{h}(x_1) \chi_2(x_1)) \\
 &= \frac{1}{2} (\langle \chi_1 | \hat{h}(x_1) | \chi_1 \rangle + \langle \chi_2 | \hat{h}(x_1) | \chi_2 \rangle) \\
 &= \langle \Psi^{SD} | \hat{h}(x_1) | \Psi^{SD} \rangle
 \end{aligned}$$

and so,

$$\begin{aligned}
 \langle \Psi^{SD} | O_1 | \Psi^{SD} \rangle &= \langle \Psi^{SD} | \hat{h}(x_1) + \hat{h}(x_2) | \Psi^{SD} \rangle \\
 &= \langle \chi_1 | \hat{h} | \chi_1 \rangle + \langle \chi_2 | \hat{h} | \chi_2 \rangle
 \end{aligned}$$

And for an N-electron wavefunction,

$$\langle \Psi^{SD} | O_1 | \Psi^{SD} \rangle = \sum_i^N \langle \chi_i | \hat{h} | \chi_i \rangle$$

where i are the orbitals occupied in Ψ^{SD}

Start of Lecture 21

- Expectation value of a 2-electron operator with a Slater Determinant wavefunction
- Again, let's start with Helium,

$$\begin{aligned}
 \langle \Psi^{SD} | \hat{v}(x_1, x_2) | \Psi^{SD} \rangle &= \frac{1}{2} \int dx_1 dx_2 [\chi_1(x_1)\chi_2(x_2) - \chi_1(x_2)\chi_2(x_1)]^* \\
 &\quad \hat{v}(x_1, x_2) [\chi_1(x_1)\chi_2(x_2) - \chi_1(x_2)\chi_2(x_1)] \\
 &= \frac{1}{2} \int dx_1 dx_2 \chi_1(1)\chi_2(2) \hat{v}(1,2) \chi_1(1)\chi_2(2) \\
 &\quad + \frac{1}{2} \int dx_1 dx_2 \chi_1(2)\chi_2(1) \hat{v}(1,2) \chi_1(2)\chi_2(1) \\
 &\quad - \frac{1}{2} \int dx_1 dx_2 \chi_1(1)\chi_2(2) \hat{v}(1,2) \chi_1(2)\chi_2(1) \\
 &\quad - \frac{1}{2} \int dx_1 dx_2 \chi_1(2)\chi_2(1) \hat{v}(1,2) \chi_1(1)\chi_2(2)
 \end{aligned}$$

In each case, we are integrating over both electron coordinates, so the first two, and last two are duplicates,

$$\begin{aligned}\left\langle \Psi^{SD} \left| \hat{v}(x_1, x_2) \right| \Psi^{SD} \right\rangle &= \int dx_1 dx_2 \chi_1(1) \chi_2(2) \hat{v}(1, 2) \chi_1(1) \chi_2(2) \\ &\quad - \int dx_1 dx_2 \chi_1(1) \chi_2(2) \hat{v}(1, 2) \chi_1(2) \chi_2(1) \\ &= \langle \chi_1 \chi_2 | \chi_1 \chi_2 \rangle - \langle \chi_1 \chi_2 | \chi_2 \chi_1 \rangle \\ &= \langle \chi_1 \chi_2 || \chi_1 \chi_2 \rangle\end{aligned}$$

where $\langle \chi_1 \chi_2 || \chi_1 \chi_2 \rangle$ is an antisymmetrized two-electron repulsion integral, when $\hat{v}(1, 2) = r_{12}^{-1}$

- For an N -electron wavefunction, there is a single matrix element for each pair of spin-orbitals

$$\begin{aligned}\left\langle \Psi^{SD} \left| r_{12}^{-1} \right| \Psi^{SD} \right\rangle &= \sum_{i < j} \langle \chi_i \chi_j | r_{12}^{-1} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | r_{12}^{-1} | \chi_j \chi_i \rangle \\ &= \sum_{i < j} \langle ij | ij \rangle = \frac{1}{2} \sum_{ij} \langle ij | ij \rangle\end{aligned}$$

- The final energy expression is therefore,

$$E^{SD} = E_N + \sum_i \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{ij} \langle \chi_i \chi_j || \chi_i \chi_j \rangle$$

7.3.2 Minimization of Energy

- How do we get the molecular orbitals, χ_i ?
- We will use the variational method. In otherwords, the best molecular orbitals are those for which the Slater determinant is orthonormalized and a minimum in energy.
- This represents a constrained optimization, and as such we will use Lagrange's method of undetermined multipliers again. However, since we don't know anything about the form of the orbitals, we will use a more general notation, and describe the Lagrangian as a functional of the orbitals.

$$\mathcal{L}[\chi_k] = E_N + \sum_i \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{ij} \langle \chi_i \chi_j || \chi_i \chi_j \rangle - \sum_{ij} \epsilon_{ij} (\langle \chi_i | \chi_j \rangle - \delta_{ij})$$

- Similar to what we've done before, we want to set the first "derivative" equal to zero. However, since this is a functional, we should refer to this as setting the first functional variation to zero, although this is mechanically identical to the derivative, i.e.,

$$\begin{aligned}\mathcal{L}[\chi_i] &\xrightarrow{\text{small change}} \mathcal{L}[\chi_i + \delta \chi_i] = \mathcal{L}[\chi_i] + \mathcal{L}[\delta \chi_i] \\ &= \mathcal{L}[\chi_i] + \delta \mathcal{L}[\chi_i]\end{aligned}$$

then require,

$$\delta \mathcal{L}[\chi_i] = 0$$

- Expand the first variation

$$\begin{aligned}\delta\mathcal{L}[\chi_k] &= \sum_i \left(\langle \delta\chi_i | \hat{h} | \chi_i \rangle + \langle \chi_i | \hat{h} | \delta\chi_i \rangle \right) \\ &\quad + \frac{1}{2} \sum_{ij} \left(\langle \delta\chi_i \chi_j | | \chi_i \chi_j \rangle + \langle \chi_i \delta\chi_j | | \chi_i \chi_j \rangle + \langle \chi_i \chi_j | | \delta\chi_i \chi_j \rangle + \langle \chi_i \chi_j | | \chi_i \delta\chi_j \rangle \right) \\ &\quad - \sum_{ij} \epsilon_{ij} (\langle \delta\chi_i | \chi_j \rangle + \langle \chi_i | \delta\chi_j \rangle) = 0\end{aligned}$$

- A couple of these terms can be combined,

$$\begin{aligned}\langle \delta\chi_i \chi_j | | \chi_i \chi_j \rangle &= \int d\mathbf{x}_1 d\mathbf{x}_2 [\delta\chi_i(1) \chi_j(2)]^* \frac{1}{r_{12}} [\chi_i(1) \chi_j(2) - \chi_j(1) \chi_i(2)] \\ &= \int d\mathbf{x}_2 d\mathbf{x}_1 [\delta\chi_i(2) \chi_j(1)]^* \frac{1}{r_{12}} [\chi_i(2) \chi_j(1) - \chi_j(2) \chi_i(1)] \quad \text{flip 1,2} \\ &= \int d\mathbf{x}_1 d\mathbf{x}_2 [\chi_j(1) \delta\chi_i(2)]^* \frac{1}{r_{12}} [\chi_j(1) \chi_i(2) - \chi_i(1) \chi_j(2)] \quad \text{reorder terms} \\ &= \langle \chi_j \delta\chi_i | | \chi_j \chi_i \rangle\end{aligned}$$

- Now, combine those terms,

$$\begin{aligned}\delta\mathcal{L}[\chi_k] &= \sum_i \left(\langle \delta\chi_i | \hat{h} | \chi_i \rangle + \langle \chi_i | \hat{h} | \delta\chi_i \rangle \right) \\ &\quad + \sum_{ij} (\langle \delta\chi_i \chi_j | | \chi_i \chi_j \rangle + \langle \chi_i \chi_j | | \delta\chi_i \chi_j \rangle) - \sum_{ij} \epsilon_{ij} (\langle \delta\chi_i | \chi_j \rangle + \langle \chi_i | \delta\chi_j \rangle) = 0\end{aligned}$$

- and separate out the complex conjugate,

$$\begin{aligned}\delta\mathcal{L}[\chi_k] &= \sum_i \langle \delta\chi_i | \hat{h} | \chi_i \rangle + \sum_{ij} \langle \delta\chi_i \chi_j | | \chi_i \chi_j \rangle - \sum_{ij} \epsilon_{ij} \langle \delta\chi_i | \chi_j \rangle + C.C. = 0 \\ &= \sum_i \int d\mathbf{x}_1 \delta\chi_i^*(1) \hat{h} \chi_i(1) + \sum_{ij} \int \int d\mathbf{x}_1 d\mathbf{x}_2 \delta\chi_i^*(1) \chi_j^*(2) \frac{1}{r_{12}} (\chi_i(1) \chi_j(2) - \chi_j(1) \chi_i(2)) \\ &\quad - \sum_{ij} \epsilon_{ij} \int d\mathbf{x}_1 \delta\chi_i^*(1) \chi_j(1) + C.C. = 0\end{aligned}$$

- Now pull out the integration over electron 1,

$$\begin{aligned}&= \sum_i \int d\mathbf{x}_1 \delta\chi_i^*(1) \\ &\quad \times \left[\hat{h} \chi_i(1) + \sum_j \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \chi_j(2) \chi_i(1) - \sum_j \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \chi_i(2) \chi_j(1) - \sum_j \chi_j(1) \epsilon_{ij} \right] \\ &\quad + C.C. = 0\end{aligned}$$

- The non-trivial solution requires the following expression to hold:

$$\begin{aligned}\hat{h}\chi_i(1) + \sum_j \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \chi_j(2) \chi_i(1) - \sum_j \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \chi_i(2) \chi_j(1) &= \sum_j \chi_j(1) \epsilon_{ij} \\ &= \left[\hat{h} + \sum_j \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \chi_j(2) - \sum_j \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \hat{P}(1,2) \chi_j(2) \right] \chi_i(1) = \sum_j \chi_j(1) \epsilon_{ij}\end{aligned}$$

- Fock operator

- The second term, can be rewritten as an effective 1-electron coulomb operator ,

$$\sum_j \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \chi_j(2) \chi_i(1) = \sum_j \hat{J}_j(1) \chi_i(1)$$

where,

$$\hat{J}_j(1) = \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \chi_j(2)$$

- The third term, can be rewritten as an effective 1-electron exchange operator ,

$$\sum_j \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \chi_i(2) \chi_j(1) = \sum_j \hat{K}_j(1) \chi_i(1)$$

where,

$$\hat{K}_j(1) = \int d\mathbf{x}_2 \chi_j(2) \frac{1}{r_{12}} \hat{P}(1,2) \chi_j(2)$$

and $\hat{P}(1,2)$ is the permutation operator, $\hat{P}(1,2) \chi_i(1) \chi_j(2) = \chi_i(2) \chi_j(1)$

- The exchange operator, \hat{K} , is a *purely quantum mechanical* quantity with no classical analogue. Because the integral over \mathbf{x}_2 takes place when electron 2 is in two different orbitals, this is commonly called non-local exchange
- We can now use these definitions to define a Fock operator, \hat{f} ,

$$\hat{f} = \hat{h}(1) + \sum_j (\hat{J}_j(1) - \hat{K}_j(1))$$

such that,

$$\hat{f} \chi_i(1) = \sum_j \epsilon_{ij} \chi_j(1)$$

this constitutes the Hartree-Fock equations

7.3.3 Canonical orbitals

- In order to transform the Hartree-Fock equations into the pseudo-eigenvalue equation, we need to consider how a Slater determinant behaves under unitary transformation.
- Consider the effect of combining all of the occupied molecular orbitals via multiplication with a **unitary matrix** (i.e., one for which $\mathbf{U}^\dagger = \mathbf{U}^{-1}$),

$$\chi'_i = \sum_j \chi_j U_{ji}$$

- Now, recall that the Slater determinant is the determinant of a matrix of orbitals with varying electron coordinates:

$$\begin{aligned}\Psi^{SD}(x_1, x_2, \dots, x_N) &= \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \chi_1(1) & \chi_1(2) & \cdots & \chi_1(N) \\ \chi_2(1) & \chi_2(2) & \cdots & \chi_2(N) \\ \vdots & & & \\ \chi_N(1) & \chi_N(2) & \cdots & \chi_N(N) \end{pmatrix} \\ &= \frac{1}{\sqrt{N!}} \det(\mathbf{A})\end{aligned}$$

- If we were to multiply this matrix \mathbf{A} by U , we would get,

$$\begin{aligned}\mathbf{AU} &= \left(\sum_j \chi_i(1) U_{ij} \mid \sum_j \chi_i(2) U_{ij} \mid \cdots \mid \sum_j \chi_i(N) U_{ij} \right) \\ &= (\chi'_i(1) \mid \chi'_i(2) \mid \cdots \mid \chi'_i(N)) \\ &= \mathbf{A}'\end{aligned}$$

- Taking the determinant of this equation, and using the fact that $\det(\mathbf{AU}) = \det(\mathbf{A}) \det(\mathbf{U})$,

$$\begin{aligned}\det(\mathbf{A}) \det(\mathbf{U}) &= \det(\mathbf{A}') \\ \left| \Psi^{SD} \right\rangle \det(\mathbf{U}) &= \left| \Psi'^{SD} \right\rangle \\ \left| \Psi^{SD} \right\rangle &= \left| \Psi'^{SD} \right\rangle\end{aligned}$$

- since, $\det(\mathbf{U}) = 1$ via,

$$\begin{aligned}\det(\mathbf{U}^\dagger \mathbf{U}) &= \det(\mathbf{I}) = 1 \\ &= \det(\mathbf{U})^\dagger \det(\mathbf{U}) \\ &= |n|^2 = 1\end{aligned}$$

- As a result, Unitary transformation of the occupied orbitals leaves the wavefunction unchanged! This means, that if χ_i are solutions to the Hartree-Fock equations, then so are χ'_i
- Now let's choose a specific unitary transformation which makes the matrix of Lagrange multipliers (ϵ_{ij}) diagonal,

$$\begin{aligned}\hat{f}\chi_i &= \sum_j \epsilon_{ij} \chi_j \\ &= \sum_{jk} U_{ik} \epsilon_k U_{kj} \chi_j \\ &= \sum_k U_{ik} \epsilon_k \chi'_k\end{aligned}$$

now, multiply both sides by U_{il} and sum,

$$\begin{aligned}\sum_i \hat{f}\chi_i U_{il} &= \sum_i \sum_k U_{il} U_{ik} \epsilon_k \chi'_k \\ \hat{f}\chi'_l &= \sum_k \delta_{lk} \epsilon_k \chi'_k \\ \hat{f}\chi'_l &= \epsilon_l \chi'_l\end{aligned}$$

- We have now arrived at the **canonical orbital** form of the Hartree-Fock equation. These are the typical orbitals that one associates with Hartree-Fock, and are delocalized throughout the molecule. It is in this form that the Lagrange multiplier has a physical significance, the energy of the one-electron orbital!

Start of Lecture 22

7.3.4 Koopman's Theorem

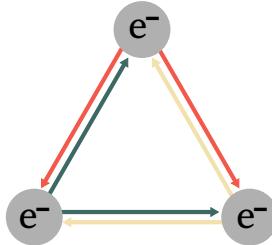
- What do the orbital “energies” mean?
- First, the sum of orbital energies does not correspond to the HF energy,

$$\begin{aligned}\epsilon_i &= \langle \chi_i | \hat{f} | \chi_i \rangle \\ &= \langle \chi_i | \hat{h} + \sum_j (\hat{j}_j - \hat{K}_j) | \chi_i \rangle \\ &= \langle \chi_i | \hat{h} | \chi_i \rangle + \sum_j \int d\mathbf{x}_1 \int d\mathbf{x}_2 \chi_i(1)^* \chi_j^*(2) r_{12}^{-1} (1 - \hat{P}(1,2)) \chi_j(2) \chi_i(1) \\ &= \langle \chi_i | \hat{h} | \chi_i \rangle + \sum_j \langle \chi_i \chi_j || \chi_i \chi_j \rangle \\ \sum_i \epsilon &= \sum_i \langle \chi_i | \hat{h} | \chi_i \rangle + \sum_{ij} \langle \chi_i \chi_j || \chi_i \chi_j \rangle\end{aligned}$$

so,

$$E^{HF} = \sum_i \epsilon_i - \frac{1}{2} \sum_{ij} \langle \chi_i \chi_j || \chi_i \chi_j \rangle$$

- Thus, we see that the sum of orbital energies double counts the electron-electron repulsions



Definition: Koopman's theorem

Occupied orbital energies, are approximations to the ionization energies.

- To illustrate this, consider the k^{th} ionization potential, $\text{IP}_k = E_k^{N-1} - E^N$

$$E^N = \sum_i \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{ij} \langle \chi_i \chi_j | | \chi_i \chi_j \rangle$$

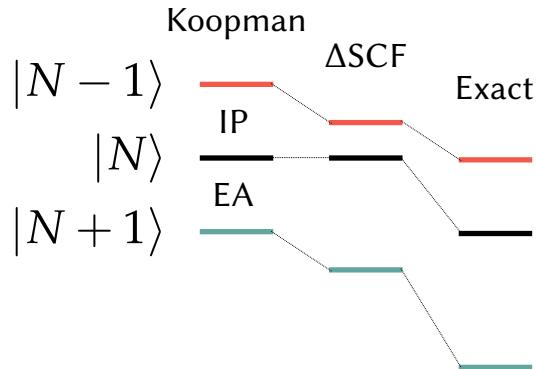
- If we make the approximation that the optimal orbitals are unchanged during the ionization process, then,

$$E_k^{N-1} = \sum_{i \neq k} \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{i \neq k, j \neq k} \langle \chi_i \chi_j | | \chi_i \chi_j \rangle$$

- Then,

$$\begin{aligned} E_k^{N-1} - E^N &= - \langle \chi_k | \hat{h} | \chi_k \rangle - \frac{1}{2} \sum_{j \neq k} \langle \chi_k \chi_j | | \chi_k \chi_j \rangle - \frac{1}{2} \sum_{i \neq k} \langle \chi_i \chi_k | | \chi_i \chi_k \rangle \\ &= - \langle \chi_k | \hat{h} | \chi_k \rangle - \sum_j \langle \chi_k \chi_j | | \chi_k \chi_j \rangle \quad \text{allowing } j = k \\ &= -\epsilon_k \end{aligned}$$

- Thus, the ionization potential associated with removing an electron from the k^{th} occupied orbital is just the negative of that orbital energy.
- A similar relationship holds for the Electron affinity, although this is often much less accurate



- This is because if orbital relaxation is included, both $|N - 1\rangle$ and $|N + 1\rangle$ states will lower in energy (Δ SCF values). However, when electron correlation is added, all states will decrease in energy. The amount of correlation depends on the number of electrons. As such, the $|N + 1\rangle$ energy will decrease the most. This ultimately leads to Koopman IP's being more accurate than Koopman EA's.

7.3.5 Solving the Hartree-Fock equations

- Notice that although the canonical HF equations look like a typical eigenvalue equation, it is not. The Fock operator depends on the solution:

$$\hat{f}[\chi_i]\chi_i = \epsilon\chi_i$$

- As a consequence, we have a non-linear optimization problem, which we solve iteratively.

1. Guess initial form of MO's, $\{\chi_i^{(it)}\}$
2. Build Fock operator with initial MO's, $\hat{f}[\chi_i^{(it)}]$
3. Find eigenvalues/vectors of $\hat{f}[\chi_i^{(it)}]$ to yield update MO's, $\chi_i^{(it+1)}$ for the next iteration
4. Did the MO's change? Compare $\chi_i^{(it)}$ and $\chi_i^{(it+1)}$
 - If Yes: Go back to step 2.
 - If No: done.

- What should the form of our molecular orbitals be? The answer to this is not obvious. The most successful strategy has been to assume that our MO's can be written as a linear combination of fixed functions. The final MO's are defined by the expansion coefficients, $C_{\mu i}$, and thus these are the variables we want to solve for.

$$\chi_i(x_1) = \sum_{\mu} \phi_{\mu}(x_1) C_{\mu i}$$

or, in Dirac notation,

$$|\chi_i\rangle = \sum_{\mu} |\phi_{\mu}\rangle C_{\mu i}$$

- This allows us to replace the complex integro-differential equation with a series of linear equations.

$$\begin{aligned} \hat{f}|\chi_i\rangle &= |\chi_i\rangle \epsilon_i \\ \sum_{\mu} \hat{f}|\phi_{\mu}\rangle C_{\mu i} &= \sum_{\nu} |\phi_{\nu}\rangle C_{\nu i} \epsilon_i \end{aligned}$$

Multiply by $\langle\phi_{\lambda}|$

$$\begin{aligned} \sum_{\mu} \langle\phi_{\lambda}|\hat{f}|\phi_{\mu}\rangle C_{\mu i} &= \sum_{\nu} \langle\phi_{\lambda}|\phi_{\nu}\rangle C_{\nu i} \epsilon_i \\ \sum_{\mu} F_{\lambda\mu} C_{\mu i} &= \sum_{\nu} S_{\lambda\nu} C_{\nu i} \epsilon_i \end{aligned}$$

$$\mathbf{FC} = \mathbf{SCe}$$

We can use symmetric orthogonalization to get rid of the overlap matrix. Right multiply by $\mathbf{S}^{-\frac{1}{2}}$

$$\begin{aligned}\mathbf{S}^{-\frac{1}{2}} \mathbf{F} \mathbf{S}^{-\frac{1}{2}} \mathbf{S}^{\frac{1}{2}} \mathbf{C} &= \mathbf{S}^{\frac{1}{2}} \mathbf{C} \mathbf{e} \\ \tilde{\mathbf{F}} \tilde{\mathbf{C}} &= \tilde{\mathbf{C}} \mathbf{e}\end{aligned}$$

Now, it's just a simple eigenvalue problem.

- What does this Fock matrix look like? Let's just use the definition of the Fock operator that we've obtained above.

$$\begin{aligned}\langle \phi_\lambda | \hat{f} | \phi_\mu \rangle &= \int d\mathbf{x}_1 \phi_\lambda^*(1) \hat{h}(1) \phi_\mu(1) \\ &\quad + \frac{1}{2} \int d\mathbf{x}_1 \phi_\lambda^*(1) \left(\sum_j \int d\mathbf{x}_2 \chi_j^*(2) \frac{1}{r_{12}} (1 - \hat{P}(1, 2)) \chi_j(2) \right) \phi_\mu(1) \\ &= h_{\lambda\mu} + \frac{1}{2} \sum_{\nu\sigma} \sum_j C_{\nu j}^* C_{\sigma j} \int \int d\mathbf{x}_1 d\mathbf{x}_2 \phi_\lambda^*(1) \phi_\nu^*(2) \frac{1}{r_{12}} (1 - \hat{P}(1, 2)) \phi_\sigma(2) \phi_\mu(1) \\ &= h_{\lambda\mu} + \frac{1}{2} \sum_{\nu\sigma} P_{\nu\sigma} \langle \phi_\lambda \phi_\nu || \phi_\mu \phi_\sigma \rangle\end{aligned}$$

where we have introduced the density matrix,

$$P_{\mu\nu} = \sum_i C_{\mu i} C_{\nu i}$$

- So the Fock matrix depends on the density matrix, which ultimately comes from the MO coefficients. We thus solve this iteratively until a self-consistent field is achieved.
- Although there are N^4 individual two-electron integrals ($\langle \phi_\mu \phi_\nu || \phi_\lambda \phi_\sigma \rangle$), for large systems, it turns out that only a linear (instead of quadratic) number of $P_{\mu\nu}$ matrix elements are asymptotically non-zero. Thus, the actual number of integrals that need to be computed is much less, and this leads to HF requiring only about $\approx N^3$ computational operations.

Start of Lecture 23

7.3.6 One-electron wavefunction basis sets

- What types of functions should we use for our basis set?
- Slater-type orbitals

$$\psi_{n\zeta}^{\text{STO}}(r) = N Y_{l,m_l}(\phi, \theta) r^{n-1} e^{-\zeta r}$$

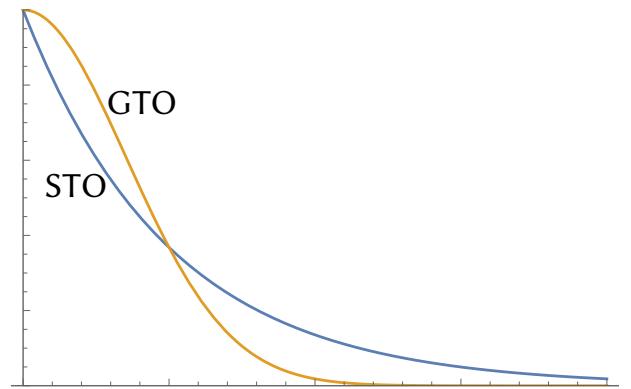
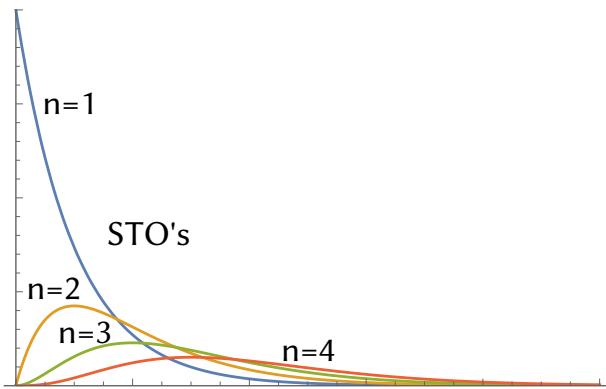
- Similar to the analytical solutions of Hydrogen, except STO's don't have radial nodes

- Become extremely complicated (and computationally demanding) when computing the 2-electron repulsion integrals, $\langle \phi_\mu \phi_\nu | \phi_\lambda \phi_\sigma \rangle$

- Gaussian-type orbitals

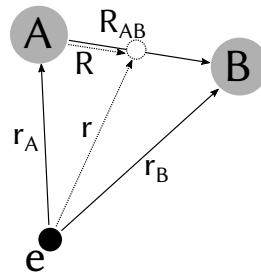
$$\psi_{n\zeta}^{\text{GTO}}(r) = N Y_{l,m_l}(\phi, \theta) e^{-\alpha r^2}$$

- Not as accurate, but efficient



- Gaussian product rule

- Consider a product of two s-type gaussian functions located on separate atoms, A and B.



- We will use the following relationships:

$$\begin{aligned}\vec{R}_{AB} &= \vec{r}_B - \vec{r}_A \\ \vec{r}_B &= \vec{R}_{AB} + \vec{r}_A \\ \vec{R} &= \vec{R}_{AB}/2 \\ \vec{r} &= \vec{r}_A + \vec{R}\end{aligned}$$

- Consider the following product of gaussian functions:

$$\begin{aligned}\phi_{\mu_A}(r_1) \phi_{\nu_B}(r_1) &\propto e^{-\alpha \vec{r}_A^2} e^{-\alpha \vec{r}_B^2} \\ &\propto e^{-\alpha \vec{r}_A^2} e^{-\alpha (2\vec{R} + \vec{r}_A)^2}\end{aligned}$$

- now, let's focus on the exponents,

$$\begin{aligned}-\alpha \vec{r}_A^2 - \alpha \left(2\vec{R} + \vec{r}_A\right)^2 &= -\alpha \vec{r}_A^2 - \alpha \left(4\vec{R}^2 + 4\vec{R} \cdot \vec{r}_A + \vec{r}_A^2\right) \\ &= -2\alpha \left(2\vec{R}^2 + 2\vec{R} \cdot \vec{r}_A + \vec{r}_A^2\right) \\ &= -2\alpha \left(\vec{R}^2 + \left(\vec{R} + \vec{r}_A\right)^2\right) \\ &= -2\alpha \vec{R}^2 - 2\alpha \vec{r}^2\end{aligned}$$

- so we see that the product of two gaussians, is itself a Gaussian, referenced to the midpoint of the two original atoms,

$$\begin{aligned}\phi_{\mu_A}(r_1)\phi_{\nu_B}(r_1) &\propto e^{-2\alpha \vec{R}^2} e^{-2\alpha \vec{r}^2} \\ &\propto A e^{-2\alpha \vec{r}^2}\end{aligned}$$

- This significantly reduces the computational cost of evaluating the numerous two-electron repulsion integrals

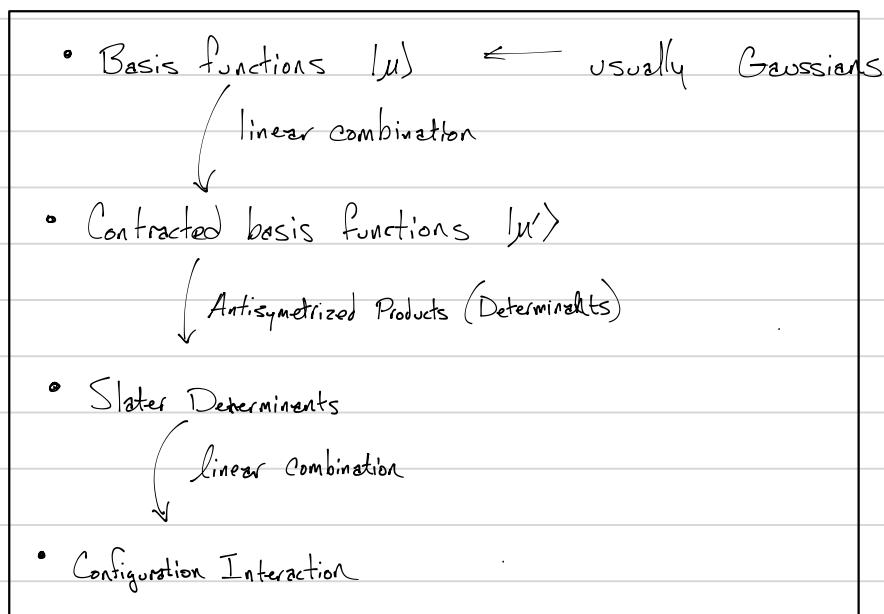
7.4 Electron Correlation

- Configuration Interaction

- HF was obtained by applying the variational method to an approximate wavefunction with the form of a Slater determinant. Consequently, the HF wavefunction is the “best” single Slater determinant wavefunction for a given system.
- As we have discussed, HF includes only the averaged interactions between electrons, with same spin electrons being statistically correlated to enforce adherence to the Pauli antisymmetry principle.
- The goal of most quantum chemistry research is focused on trying to obtain a better wavefunction (beyond HF) which includes electron correlation.

- CI -

- HF gets "most" of the energy — remaining is "correlation energy"
- What is missing from HF? — electrons avoiding each other
- $\xrightarrow{\text{HF}}$ Exact \leftarrow HF is variational, correlation is negative
- Based solely on variational principle, it's clear that an optimized linear combinations of determinants would lower energy -
- Consider H Matrix: $\boxed{\text{H}}$ = \rightarrow $\underline{\underline{\text{H}}}$ of diagonal matrix elements increase the geps!
 - any additional determinant can only decrease energy.
- Example: $\bullet \bullet \rightarrow \cancel{\bullet \bullet} \quad \leftarrow$ best single config.
- $\uparrow \downarrow + \uparrow \downarrow + \uparrow \downarrow + \uparrow \downarrow \quad \leftarrow$ electrons have more "options" to help avoid one another
- Configuration Interaction: $|\Psi\rangle = \sum_j C_j |\psi_j\rangle \quad \leftarrow$ optimize C_j



- CI - cont...

- Which determinants?

- All \rightarrow Full CI

• almost always impossible

- Most "coupled" to HF \rightarrow categorize based on number of excitations "substitutions"

$$|\Psi\rangle = C_0 |\psi_0\rangle + \sum_{i=1}^N C_i^{\text{Singles}} |\psi_i^{\text{a}}\rangle + \sum_{i,j} C_{ij}^{\text{ab}} |\psi_{ij}^{\text{ab}}\rangle + \sum_{i,j,k} C_{ijk}^{\text{abc}} |\psi_{ijk}^{\text{abc}}\rangle + \dots$$

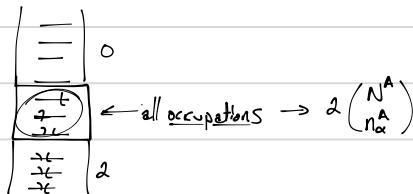
• only $\langle \psi_0 | \hat{A} | \psi_{ij}^{\text{ab}} \rangle \neq 0$ (Brilliant's theorem)

• Works well with SC rules

• CIS, CISD, CISDT, etc ...

• Works well when HF is good.

- All involving certain orbitals \rightarrow CAS-CI

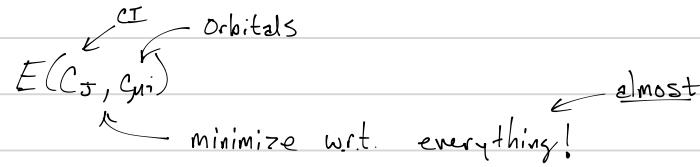


• Expensive 18 orbs max (but DMRG can help)

• Difficult to choose active orbitals

• Works when HF completely fails

• often performed in conjunction with orbital optimization CASSCF



• Very slow convergence for dynamical correlation energy

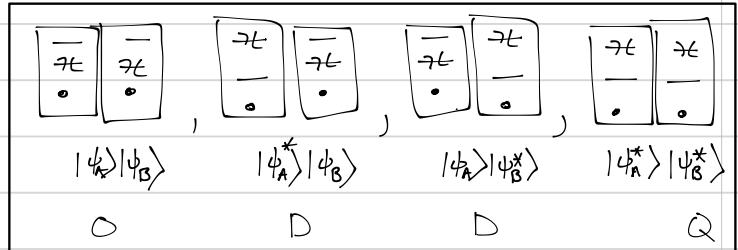
— gets strong correlation

Start of Lecture 24

— Size Consistency —

- Energy of two systems separated by ∞ should be the sum of the two systems.

- Consider He_2 : apply CISD



- $E^{\text{CID}}(\text{He}_2) \neq 2E^{\text{CID}}(\text{He})$

- More generally, CI is not size extensive \leftarrow large molecule limit approaches HF!

- Size Consistency is extremely important

- What if we do something odd \leftarrow exponentiate the wavefunction parameters...

- CI $\rightarrow |\bar{\psi}\rangle = \sum_j C_j \hat{E}_j |\psi_0\rangle^{\text{HF}} = \sum_j \hat{R}_j |\psi_0\rangle$

- CC $\rightarrow |\bar{\psi}\rangle = e^{\sum_j \hat{T}_j} |\psi_0\rangle$

- CC is size consistent ($|\bar{\psi}\rangle = |\psi_{A+B}\rangle = |\psi_A\rangle|\psi_B\rangle$)

- $|\bar{\psi}_{A+B}\rangle^{\text{CI}} = \hat{R} |\psi_{A+B}\rangle^{\text{HF}} = (\hat{R}_A + \hat{R}_B) |\psi_A\rangle |\psi_B\rangle = |\psi_A\rangle^{\text{CI}} |\psi_B\rangle^{\text{HF}} + |\psi_A\rangle^{\text{HF}} |\psi_B\rangle^{\text{CI}} \neq |\psi_A\rangle^{\text{CI}} |\psi_B\rangle^{\text{CI}}$

- $|\bar{\psi}_{A+B}\rangle^{\text{CC}} = e^{\hat{T}} |\psi_0\rangle = e^{\hat{T}_A + \hat{T}_B} |\psi_A\rangle |\psi_B\rangle = e^{\hat{T}_A} |\psi_A\rangle e^{\hat{T}_B} |\psi_B\rangle = |\bar{\psi}_A\rangle^{\text{CC}} |\bar{\psi}_B\rangle^{\text{CC}}$ ✓

- CC includes higher-order excitations (Taylor Series)

$$e^{\hat{T}} |\psi_0\rangle = \left(1 + \frac{\hat{T}}{1!} + \frac{1}{2!} \frac{\hat{T}^2}{2!} + \frac{1}{3!} \frac{\hat{T}^3}{3!} + \dots \right) |\psi_0\rangle$$

- How do we solve for the non-linear wavefunction? Variational is hard.

$$\hat{H}e^{\hat{T}}|\psi_0\rangle = E^{cc} e^{\hat{T}}|\psi_0\rangle$$

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} |\psi_0\rangle = \bar{H} |\psi_0\rangle = E^{cc} |\psi_0\rangle \quad | \quad \bar{H} \leftarrow \text{Sim. Trans. Ham.}$$

$$\langle \psi_0 | \bar{H} | \psi_0 \rangle = E^{cc} \quad \leftarrow \text{Energy expression}$$

$$\langle \psi_{ij}^{ab} | \bar{H} | \psi_0 \rangle = 0 \quad \leftarrow \text{enough equations to solve for wavefunction}$$

- Baker-Campbell-Hausdorff expansion

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2!} [[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{3!} [[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}]] + \dots$$

- Because of the 2-particle nature of H this truncates naturally after order 4.
- finite expansion, but still complex!

-
- HF $\mathcal{O}(N^4)$ ← formally
 - CISD, CCSD $\mathcal{O}(N^6)$
-

-MBPT-

- CI, CC both recover electron correlation
- Minimal (most common) examples include single & double excitations
- CISD, CCSD $\rightarrow O(N^6)$, pretty expensive
- Instead of using CI or CC, let's try perturbation theory
- Assumption: Hartree-Fock is qualitatively correct.

$$\hat{H} = H^{(0)} + \lambda H^{(1)} = \hat{F} + \lambda \hat{V} = \sum_i \hat{f}_i + \lambda \hat{V}$$

$$\hat{V} = \hat{H} - \hat{F} \leftarrow \text{"fluctuation potential"}$$

$$\text{Recall from chapt 4 : } E^{(1)} = \sum_{n \neq 0} \frac{|\langle \phi_0 | H^{(1)} | n \rangle|^2}{E_0^{(0)} - E_n^{(0)}}$$

- Remember $|n\rangle$ is an excited state of $\hat{H}^{(0)}$

\swarrow higher order excitations don't mix

$$|n\rangle = |\psi_{ij}^{ab}\rangle, \quad |\psi\rangle^{(1)} = \sum_n C_n^{(1)} |n\rangle = \sum_{i,j,a,b} C_{ij}^{ab} |\psi_{ij}^{ab}\rangle$$

$$\langle \phi_0 | V | n \rangle = \langle \phi_0 | \hat{H} | \psi_{ij}^{ab} \rangle - \langle \phi_0 | \hat{F} | \psi_{ij}^{ab} \rangle = \langle \phi_0 | \phi_i + \phi_j | \psi_{ij}^{ab} \rangle \quad (D_0 E^{(1)} = \langle \phi_0 | V | \phi_0 \rangle = E^{HF} - \sum_m E_m^{(0)} E^{(1)m} E^{HF})$$

$$= \int dx_i dx_j \chi_i^{*(1)} \chi_j^{*(1)} \frac{1}{r_{ij}} (\chi_a(1) \chi_b(2) - \chi_a(2) \chi_b(1)) = \langle ij||ab \rangle$$

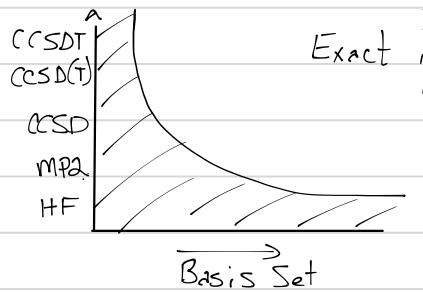
$$E_0^{(0)} = \langle \phi_0 | \sum_m f(m) | \phi_0 \rangle = \sum_i \langle i | i | i \rangle = \sum_i \epsilon_i$$

$$E_n^{(0)} = \langle n | \sum_m f(m) | n \rangle = \langle \psi_{ij}^{ab} | \sum_m f(m) | \psi_{ij}^{ab} \rangle = E_0^{(0)} - \epsilon_i - \epsilon_j + \epsilon_a + \epsilon_b$$

$$E_0^{(1)} = \sum_{i,j} \sum_{a < b} \frac{|\langle ij||ab \rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} = \frac{1}{4} \sum_{i,j} \frac{|\langle ij||ab \rangle|^2}{\Delta_{ij}^{ab}} \quad \leftarrow \langle \mu\nu||\lambda\sigma \rangle C_{\mu\nu} = \langle i\nu||\lambda\sigma \rangle \quad O(N^5)$$

Method	Variational	Size Consistent	Cost	Accuracy
HF	✓	✓	$\Theta(N^4)^*$	Not Really
MP2	X	✓	$\Theta(N^5)$	kinda
CISD	✓	X	$\Theta(N^6)$	kinda
CCSD	X	✓	$\Theta(N^6)$	yes
CCSD(T)	X	✓	$\Theta(N^7)$	<u>yes!</u>

- "Pople diagram"



- Extrapolation Schemes:

- example:

$$E \approx E_{TZ}^{CCSDT} + E_{QZ}^{MP2} - E_{TZ}^{MP2}$$

- many schemes

- G2, G3, G4 ...

- CBS

- Wn

- HEAT

- cc-CA

7.4.1 DFT

- Although we know that the exact energy (or any observable) can be obtained if we have found the exact wavefunction, is there a simpler way? Density functional theory (DFT) provides a simpler approach to solving the Schrödinger equation using the electron density as the central quantity instead of the wavefunction.
- Start with the normalization criterion,

$$1 = \int dx_1 dx_2 \cdots dx_N \psi^*(x_1 x_2 \cdots x_N) \psi(x_1 x_2 \cdots x_N)$$

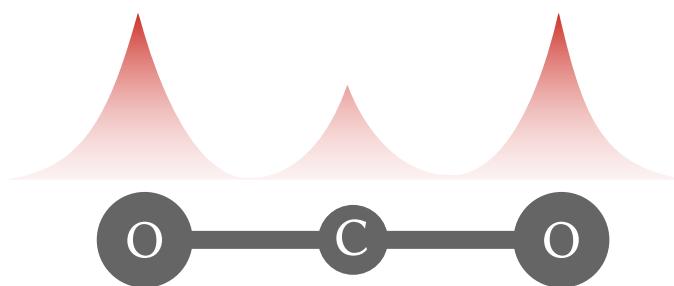
and then carry out the integrations over all coordinates except x_1 ,

$$1 = \frac{1}{N} \int dx_1 \rho(x_1)$$

where the one-electron reduced density $\rho(x_1)$ is,

$$\rho(x_1) = \int dx_2 \cdots dx_N \psi^*(x_1 x_2 \cdots x_N) \psi(x_1 x_2 \cdots x_N)$$

- Although $\rho(x_1)$ depends only on a single electron's coordinates, it can tell us a lot:
 - The integration of the density yields number of electrons
 - The positions of the cusps tell us where the nuclei are located
 - The height of the cusps tell us the nuclear charge of the atom



- In terms of complexity, the density (a function of only 3 coordinates) is a much simpler quantity than the wavefunction (a function of $3N$ coordinates)
- DFT asserts that the energy is a functional of the density, $E[\rho(x_1)]$, and that we should search for the form of the functional, then find the density. The following theorem makes this possible.

Definition: Hohenberg-Kohn Theorem 1

- The ground-state density ρ uniquely determines the ground state energy/properties
- To prove that $E \leftrightarrow \rho$ (or equivalently that $\hat{H} \leftrightarrow \rho$) we must show that

1. the Hamiltonian has a one-to-one correspondence with the ground state wavefunction
2. the wavefunction has a one-to-one correspondence with the density

– Assume we have two Hamiltonians

$$\begin{aligned}\hat{H} &= -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_A \frac{Z_A}{r_{iA}} + \sum_{i < j} \frac{1}{r_{ij}} \\ &= -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i v_{ext}(r_i) + \sum_{i < j} \frac{1}{r_{ij}}\end{aligned}$$

$$\hat{H}' = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i v'_{ext}(r_i) + \sum_{i < j} \frac{1}{r_{ij}}$$

where the external potentials differ by more than a constant,

$$v_{ext} \neq v'_{ext} + c$$

such that

$$\begin{aligned}\hat{H} |\psi\rangle &= E_0 |\psi\rangle \\ \hat{H}' |\psi'\rangle &= E'_0 |\psi'\rangle\end{aligned}$$

– By the variational principle we know that,

$$\begin{aligned}E_0 &< \langle \psi' | \hat{H} | \psi' \rangle \\ &< \langle \psi' | \hat{H}' | \psi' \rangle + \langle \psi' | \hat{H} - \hat{H}' | \psi' \rangle \\ &< E'_0 + \sum_i \langle \psi' | [v_{ext}(r_i) - v'_{ext}(r_i)] | \psi' \rangle \\ &< E'_0 + \sum_i \int d\mathbf{x}_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \psi'^*(\mathbf{x}_1 \mathbf{x}_2 \dots) [v_{ext}(r_i) - v'_{ext}(r_i)] \psi'(\mathbf{x}_1 \mathbf{x}_2 \dots) \\ &< E'_0 + \sum_i \int d\mathbf{x}_i \frac{1}{N} \rho'(\mathbf{x}_i) [v_{ext}(r_i) - v'_{ext}(r_i)] \\ &< E'_0 + \int dr_1 \rho'(r_1) [v_{ext}(r_1) - v'_{ext}(r_1)] \quad \text{sum}\end{aligned}$$

– Likewise,

$$E'_0 < E_0 - \int dr_1 \rho(r_1) [v_{ext}(r_1) - v'_{ext}(r_1)]$$

– Now, suppose $v_{ext} \neq v'_{ext}$ but $\rho = \rho'$

$$\begin{aligned}E'_0 &< E_0 + \int dr_1 \rho(r_1) \hat{\Delta}(r_1) \\ E_0 &< E'_0 - \int dr_1 \rho(r_1) \hat{\Delta}(r_1)\end{aligned}$$

leading to,

$$E'_0 - E_0 < E'_0 - E_0$$

which tells us that our supposition was not possible.

- Consequently,

$$E[\rho] = T[\rho] + V_{ee}[\rho] + \int \rho(r_1) v_{ext}(r_1) dr_1$$

where we now define the **Hohenberg-Kohn universal functional**

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho]$$

- Now that we know that the energy is indeed a functional of the density, how do we find the density?

Definition: Hohenberg-Kohn Theorem 2

- Any trial density $\rho'(r)$, the energy of that density is an upper bound the exact ground state density

$$\begin{aligned} E[\rho] &= \langle \psi | \hat{H} | \psi \rangle \leq \langle \psi' | \hat{H} | \psi' \rangle = E[\rho'] \\ E[\rho] &\leq E[\rho'] \end{aligned}$$

Start of Lecture 26

7.4.2 Kohn-Sham DFT

- What should the kinetic energy functional look like? This is a hard question. Solve it and you will probably get a Nobel prize. A simple (and very inaccurate) approximation that is based on the homogeneous electron gas is called the Thomas-Fermi functional,

$$E_{TF} = \frac{3}{10} \left(3\pi^2\right)^{\frac{2}{3}} \int [\rho(r)]^{\frac{5}{3}} d^3r.$$

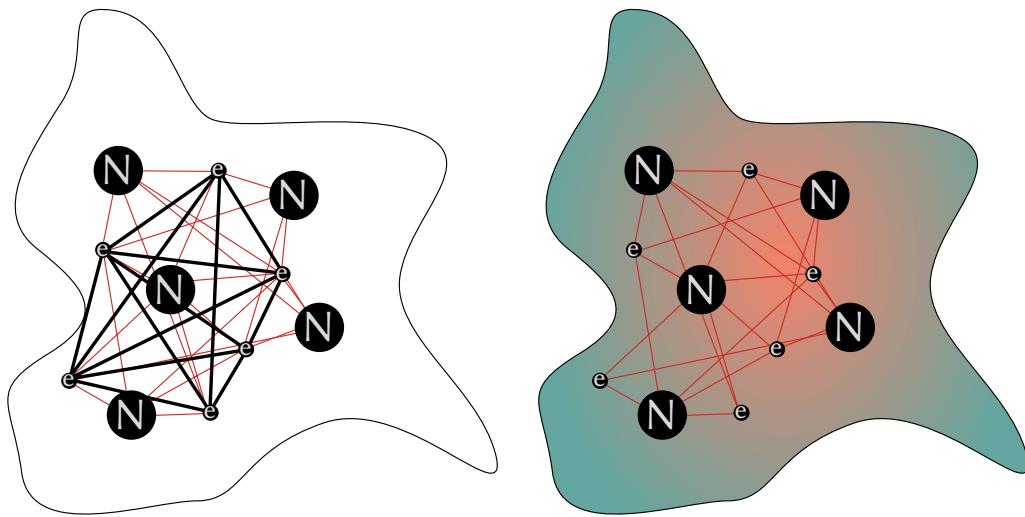
- **Kohn-Sham DFT** provides a much more accurate approach for evaluating the kinetic energy.
- *What if* we assumed that the system was non-interacting, such that the exact wavefunction happened to be a single Slater determinant?

- In other words, assume we know how to modify the external potential such that we can delete the electron-electron repulsion, and **still get the same density**

$$\begin{aligned}\hat{H}_\lambda &= \hat{T} + \lambda \hat{V}_{ee} + \hat{V}_{ext}(\lambda) \\ &= \sum_i \hat{h}^{\text{KS}}(r_i) \quad \text{when } \lambda \rightarrow 0 \\ &= \sum_i -\frac{1}{2} \nabla_i^2 + \hat{V}_{ext}(0)\end{aligned}$$

where $\hat{V}_{ext}(0)$ corresponds to some fictitious external potential energy, and where $\hat{V}_{ext}(1) = \hat{V}_{eN}$

- As a one-particle operator, a single Slater determinant provides an exact solution. The spin-orbitals that form this determinant are called **Kohn-Sham orbitals**, $\chi_i^{\text{KS}}(x_1)$



- The kinetic energy would simply be the expectation value of the kinetic energy operator:

$$\begin{aligned}T_s[\rho] &= - \langle \psi | \sum_i \frac{1}{2} \nabla^2 | \psi \rangle \\ &= - \frac{1}{2} \sum_i \langle \chi_i^{\text{KS}} | \nabla^2 | \chi_i^{\text{KS}} \rangle\end{aligned}$$

- the s subscript indicates that this is only the form of the functional when the state is a single Slater determinant.
- Unfortunately, the system is **not** non-interacting, and thus $T[\rho] \neq T_s[\rho]$
- However, $T_s[\rho]$ gets “most” of the kinetic energy, and it becomes helpful to write the kinetic energy as $T_s[\rho]$ plus a small correction:

$$T[\rho] = T_s[\rho] + (T[\rho] - T_s[\rho])$$

- Further, we can easily write down the $V_{ee}[\rho]$ functional, as a sum of the classical electron-electron repulsion functional and a correction:

$$J[\rho] = \int dr_1 dr_2 \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|}$$
$$V_{ee}[\rho] = J[\rho] + (V_{ee}[\rho] - J[\rho])$$

- Finally, returning to the original energy functional, we can substitute these values in:

$$E[\rho] = T_s[\rho] + (T[\rho] - T_s[\rho]) + J[\rho] + (V_{ee}[\rho] - J[\rho]) + \int \rho(r_1) v_{ext}(r_1) dr_1$$
$$= T_s[\rho] + J[\rho] + \int \rho(r_1) v_{ext}(r_1) dr_1 + E_{xc}[\rho]$$

7.5 Excited States

7.5.1 Born-Oppenheimer Approximation

- In all of the previous examples, we were talking about calculating the ground states. What about excited electronic states? This language already assumes that we can talk about the electronic degrees of freedom, and the nuclear degrees of freedom separately. Let's develop this idea more carefully.
- The mass of proton is ≈ 2000 x as large as an electron. As such, for a given amount of kinetic energy, the electron moves about 45x faster than a proton. Perhaps we should expect different timescales.

Adiabatic & Born-Oppenheimer Approximations

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{NN} + \hat{V}_{ee}$$

Let,

$$\hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{Ne} + \hat{V}_{NN}$$

$$\hat{H} = \hat{H}_e + \hat{T}_N + \hat{H}_{mp}$$

$$\hat{T}_N = \sum_A \frac{-1}{2m_A} \nabla_A^2$$

$$H_{mp} = -\frac{1}{2M_{tot}} \left(\sum_i \nabla_i^2 \right)^2$$

$$\Psi(R, r) = \sum_K C_K(R) \psi_e(R, r) = \sum_K \phi_{NK}(R) \psi_K(R, r)$$

where

$$\hat{H}_e \Psi(R, r) = E_e(R) \Psi(R, r)$$

$$\hat{H} \Psi(R, r) = E \Psi(R, r)$$

$$= E \sum_K \phi_{NK}(R) \psi_K(r; R)$$

$$\hat{H} \Psi = \sum_K (\hat{T}_N + \hat{H}_e + \hat{H}_{mp}) \phi_{NK} \psi_K = \sum_K E \phi_{NK} \psi_K$$

$$\langle \Psi | \hat{H} | \Psi \rangle = \sum_K \left(\sum_A \frac{-1}{2m_A} \nabla_A \nabla_A \phi_{NK} \psi_K + E_K \phi_{NK} \psi_K + \hat{H}_{mp} \phi_{NK} \psi_K \right) =$$

$$= \sum_K \left(\sum_A \frac{-1}{2m_A} \nabla_A (\phi_{NK} \nabla_A \psi_K + \psi_K \nabla_A \phi_{NK}) + \dots \right)$$

$$= \sum_K \left(\sum_A \frac{-1}{2m_A} \left[(\nabla_A \phi_{NK})(\nabla_A \psi_K) + \phi_{NK} \nabla_A^2 \psi_K + \psi_K \nabla_A^2 \phi_{NK} \right] + E_K \phi_{NK} \psi_K + \phi_{NK} \hat{H}_{mp} \psi_K \right)$$

$$\langle \psi_j | \hat{H} | \Psi \rangle_r = \sum_K \left(\sum_A \frac{-1}{2m_A} \left[2 \langle \psi_j | \nabla_A | \psi_K \rangle \cdot \nabla_A \phi_{NK} + \phi_{NK} \langle \psi_j | \nabla_A^2 | \psi_K \rangle + \nabla_A^2 \phi_{NK} \delta_{kj} + \sum_l \phi_{NK} \delta_{kj} \right] + \phi_{NK} \langle \psi_j | \hat{H}_{mp} | \psi_K \rangle \right) =$$

$$\langle \psi_j | H | \Psi \rangle_c = \left(\sum_A \frac{1}{2m_A} (\nabla_A^2 + E_j^0) \right) \phi_{Nj} + \sum_K \left[\sum_A -\frac{1}{2m_A} \left(2 \langle \psi_j | \nabla_A | \psi_K \rangle \cdot \nabla_A \phi_{NK} + \langle \psi_j | \nabla_A^2 | \psi_K \rangle \phi_{NK} \right) + \langle \psi_j | \hat{H}_{\text{imp}} | \psi_K \rangle \phi_{NK} \right]$$

$$= E^{\text{tot}} \phi_{Nj}$$

$$\left[\hat{T}_N + E_j(R) \right] \phi_{Nj} + \sum_K \left[\sum_A -\frac{1}{2m_A} \left(2 \langle \psi_j | \nabla_A | \psi_K \rangle \cdot \nabla_A + \langle \psi_j | \nabla_A^2 | \psi_K \rangle \right) + \langle \psi_j | \hat{H}_{\text{imp}} | \psi_K \rangle \right] \phi_{NK}$$

$$= E^{\text{tot}} \phi_{Nj}$$

• still exact

Adiabatic Approximation

$$\Psi \approx \phi_{Ni} \psi_i \quad [\text{only 1 state included}]$$

$$\left[\hat{T}_N + E_j(R) \right] \phi_{Nj} + \left[2 \sum_A \frac{1}{2m_A} \langle \psi_j | \nabla_A | \psi_i \rangle \nabla_A + \langle \psi_j | \hat{T}_N | \psi_i \rangle + \langle \psi_j | \hat{H}_{\text{imp}} | \psi_i \rangle \right] \phi_{Nj}$$

$\rightarrow 0$ odd function

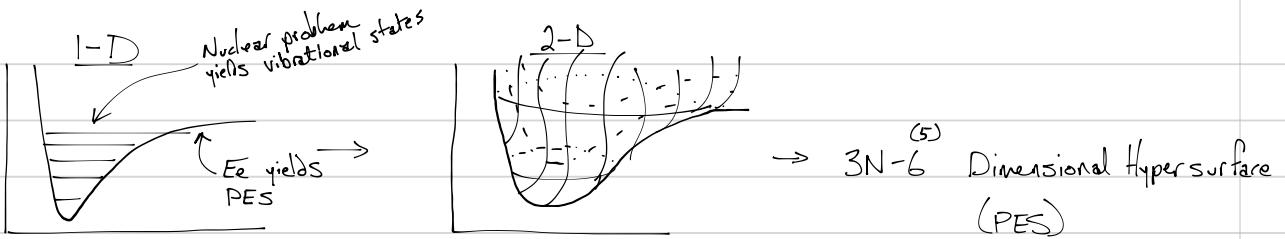
$$\left[\hat{T}_N + E_j(R) + \langle \psi_j | \hat{T}_N + \hat{H}_{\text{imp}} | \psi_i \rangle \right] \phi_{Nj} = E^{\text{tot}} \phi_{Nj}$$

Neglect \hat{H}_{imp}

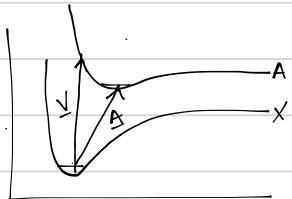
$$\left[\hat{T}_N + E_j(R) + \langle \psi_j | \hat{T}_N | \psi_j \rangle \right] \phi_{Nj} = E^{\text{tot}} \phi_{Nj}$$

↓ Born-Oppenheimer Approximation

$$\left[\hat{T}_N + E_j(R) \right] \phi_{Nj}(R) = E^{\text{tot}} \phi_{Nj}(R)$$



- But this is a function for only a single electronic energy



- Franck-Condon Principle: Since nuclei are so much heavier (and thus slower) electronic excitations can be thought of as happening instantaneously. Thus, the nuclear wavefunction, ψ_n , is unchanged during excitation.

- Recall that the probability of a given transition depends on $\langle \psi_i | \hat{v} | \psi_f \rangle$

- for a "vibronic" state transition, we need $\langle e\hat{v}\hat{e}|e\hat{v}'\hat{e}' \rangle$ to be large

$$\hat{\mu} = \hat{\mu}_e + \hat{\mu}_n \rightarrow \langle e\hat{v}\hat{e}|(\hat{\mu}_e + \hat{\mu}_n)|v'\rangle|e\rangle$$

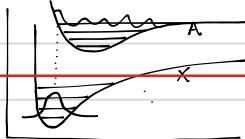
$$\bullet \text{Remember that } |v\rangle = \psi_n(r) + |e\rangle = \psi_e(r, R)$$

$$\langle e\hat{v}\hat{e}|e\hat{v}'\hat{e}' \rangle = \langle v|v'\rangle \langle e|\psi_e e'\rangle + \underbrace{\langle e|e'\rangle \langle v|\hat{\mu}_n|v'\rangle}_{\text{Not zero since } e\text{ states of different Hamiltonians}} = \langle v|v'\rangle_{M_e, e'}$$

Not zero since e states of different Hamiltonians

○ since eigenstates of same \hat{H}

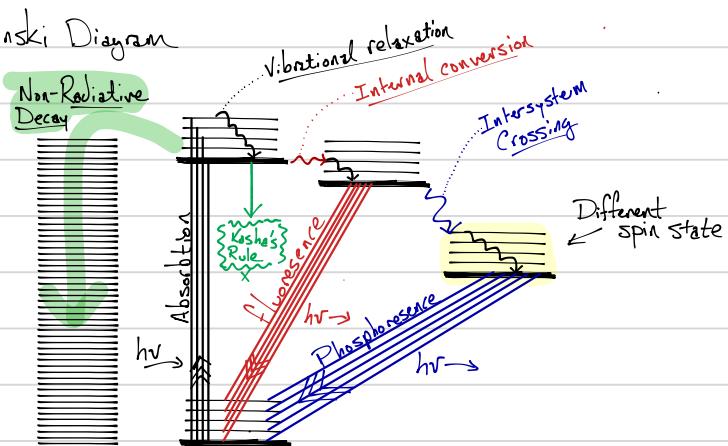
- Franck-Condon factors $\rightarrow |\langle v|v'\rangle|^2$



- Often Initial state overlaps most strongly with excited vibrational state Mayhall 130

— Jablonski Diagram —

- Franck-Condon Factors then lead to greater intensity for some vibrational states
- What happens after excitation?
 - a) Non radiative decay
 - b) fluorescence
 - c) Phosphorescence

• Jablonski Diagram• Approximate time scales

- | | |
|-----------------------------|-----------------------|
| • Absorption | ~ 1 femto second |
| • Vibrational relaxation/IC | ~ 1 pico second |
| • Fluorescence | ~ 1 nano second |
| • Phosphorescence | ~ 1 millisecond |

— CIS — (TD-DFT)

- How can we calculate the excited states?
- Just calculate higher energy levels of H matrix
- Full CI \rightarrow obviously
- CISD \rightarrow Not Good, GS has dynamic correlation, but excited states don't!
gaps too large
- CCSD \rightarrow how? one simple way \rightarrow find eigenvalues of $\tilde{H} = \hat{e}^T \hat{H} \hat{e}^T$ in basis of single + double excitations: EOM-CCSD

- Simplest: CIS

$$\psi^{\text{CIS}} = |0\rangle + \sum_{i,j} b_{ij} |\psi_{ij}\rangle$$

- Diag full matrix not good:

$H_{ia,ib} \leftarrow$ dimension $N^2 \times N^2$

Diagonalization $\leftarrow m^3$, but $m=N^2$ so cost is $N^6!$

- Normally, we only want a few of the lowest energy eigenstates.

- Use matrix-free algorithms (Davidson, Lanczos, etc.)

$$[\square] \square = \square \quad \text{cost determined by Matrix vector multiply}$$

$$\bullet H_{ia,jb} b_{jb} = \langle i|j\rangle b_{jb} = \langle a||jb\rangle b_{jb} \quad \leftarrow \text{why is this not } N^5 \text{ like MP2}$$

$$\sigma_{ai} = \langle a||jb\rangle b_{jb} = \langle u v || \lambda \sigma \rangle C_{ua} C_{vj} C_{\lambda i} C_{\lambda b} b_{jb} = \langle u v || \lambda \sigma \rangle C_{ua} C_{\lambda i} \tilde{P}_{v\sigma} = \tilde{F}_{u\lambda} C_{ua} C_{\lambda i} = \sigma_{ai}$$

$\hookrightarrow N^4$ just like Hartree-Fock!

8 Appendix

8.1 Properties of the Fourier transform

Definition: Fourier transform

The form of the Fourier transform used can vary slightly. Here are a few for 1D (3D is just the same but with $(2\pi\hbar)^{-3/2}$):

$$\mathcal{F}[f(x)] = \bar{f}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int f(x) e^{-ipx/\hbar} dx$$

$$\mathcal{F}[\bar{f}(p)] = f(x) = \frac{1}{\sqrt{2\pi\hbar}} \int \bar{f}(p) e^{ipx/\hbar} dp$$

other defs.

$$\mathcal{F}[f(x)] = \bar{f}(k) = \int f(x) e^{-2\pi i k x} dx$$

$$\mathcal{F}[f(x)] = \bar{f}(k) = \frac{1}{\sqrt{2\pi\hbar}} \int f(x) e^{-ikx/\hbar} dx \quad \text{with Planck's const}$$

The square root of 2π is the chosen form for symmetry purposes. Using the time-scaling property, one could expect to see the constant without the $\sqrt{\cdot}$. The forward and backward transforms would then look a bit different, but still just as good.

The Fourier transform between variables x and k has the following properties (using the first definition):

1. Linearity

$$\begin{aligned} \text{if } h(x) &= af(x) + bg(x) & \forall a, b \in \mathbb{C} \\ \text{then } \bar{h}(k) &= a\bar{f}(k) + b\bar{g}(k) \end{aligned}$$

2. Translation/Time-shifting

$$\begin{aligned} \text{if } h(x) &= f(x - x_0) & \forall x_0 \in \mathbb{R} \\ \text{then } \bar{h}(k) &= e^{-ikx_0} \bar{f}(k) \end{aligned}$$

3. Modulation/Frequency-shifting

$$\begin{aligned} \text{if } h(x) &= e^{ik_0 x} f(x) & \forall k_0 \in \mathbb{R} \\ \text{then } \bar{h}(k) &= \bar{f}(k - k_0) \end{aligned}$$

4. Time scaling

$$\begin{aligned} \text{if } h(x) &= f(ax) & \forall a > 0 \in \mathbb{R} \\ \text{then } \bar{h}(k) &= \frac{1}{|a|} \bar{f}\left(\frac{k}{a}\right) \end{aligned}$$

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