\[ \langle \psi | (x_1 - x_2)^2 | \psi \rangle = \langle \psi | x_1^2 | \psi \rangle + \langle \psi | x_2^2 | \psi \rangle - 2 \langle \psi | x_1 x_2 | \psi \rangle + 2 \langle \psi | x_1 | \psi \rangle \langle \psi | x_2 | \psi \rangle \]

**fermion case**

boson case

\[ \langle \psi | (x_1 - x_2)^2 | \psi \rangle = \langle \psi | x_1^2 | \psi \rangle + \langle \psi | x_2^2 | \psi \rangle - 2 \langle \psi | x_1 x_2 | \psi \rangle + 2 \langle \psi | x_1 | \psi \rangle \langle \psi | x_2 | \psi \rangle \]

the fermions are "pushed apart" relative to the bosons

but note there was no force between them in Hamiltonian

Non-interacting particles interact then exchange

- When \( \langle \psi | x_1 x_2 | \psi \rangle \neq 0 \), exchange doesn't matter.
- the real case
  - fermions have spin as well as space
  - bosons can have spin

- full state has spinor and spatial wave function

Exchange (P) means exchange everything not just space

eg basis states for single spin \( \frac{1}{2} \)

\( | r \uparrow, m \rangle \) mirror states

2 particle states (distinguishable)

\( | r_1, m_1, r_2, m_2 \rangle \)

Now \( P | r_1, m_1, r_2, m_2 \rangle = | r_2, m_2, r_1, m_1 \rangle \)

if identical \( | r_1, m_1, r_2, m_2 \rangle = - | r_2, m_2, r_1, m_1 \rangle \)

what is \( | r_1, m_2, r_2, 0 \rangle \) not immediately related to above unless \( m_1 = m_2 \)
eq. 2 spin ½ particles

\[ \psi_a(\mathbf{r}) \psi_a(\mathbf{r}) \]

\[ \psi_b(\mathbf{r}) \psi_b(\mathbf{r}) \]

\[ \psi_a(\mathbf{r}) \psi_b(\mathbf{r}) \]

\[ \psi_b(\mathbf{r}) \psi_a(\mathbf{r}) \]

\[ x_1 \times x_3 \pm x_3 \times x_1 \]

combine space-spin (sym-anti) or anti-sym

more generally

\[ [\psi(r_s, r_a) \pm \psi(r_a, r_s)] [x_1 \times x_3 \pm x_3 \times x_1] \]

Note if space is symmetric then spin anti-sym

but anti-sym means total \( L = 0 \)

if space is anti-symmetric then spin sym

which means total spin \( L = 1 \)

Consider He atom: two electrons

if two electrons are \( L = 0 \) (para helium)

\( \psi \) has symmetric space wave functions

(both electrons can be in same state spatially)
Now our lowest energy has both electron in lowest orbital space is symmetric and spin is anti sym (so)

ortho He has greater energy than para

Periodic Table

Free Fermi gas (cond. mat. phys. astrophys.)

\[ V(x) = \begin{cases} \infty & x < 0 \\ 0 & \text{otherwise} \end{cases} \]

no interactions between fermions

gross spin for new

Single particle levels

\[ E_{\text{single}} = \frac{\hbar^2 k^2}{2m} \quad \text{for} \quad \kappa \gg 1 \]

\[ E = \sum_{j=1}^{N} \frac{k_j^2}{2m} \quad \text{(up to} \quad \frac{1}{N} \text{corrections)} \]

\[ E \approx \int_0^\infty \frac{k^2}{2m} dk - \frac{L}{\pi} \int_0^\infty \frac{k^2 + k_0^2}{2m} dk \]

\[ E = \frac{\epsilon}{2} \quad \text{more useful} \]

\[ E = \frac{1}{\pi \hbar^2} \quad \text{particle density} \quad \rho = \frac{N}{V} = \frac{\kappa_0}{\pi} \]

\[ \epsilon = \frac{1}{2} m \hbar \omega \]
\[ E = 2 \sum_{j' > 0} \left[ \frac{h^2}{2m} \left( \frac{x_j^2 + y_j^2 + z_j^2}{2m} \right) \right] \]

\[ E = 2 \int \frac{d^3k}{(2\pi)^3} \theta(k_x^2 + k_y^2 + k_z^2) \frac{k_x^2 + k_y^2 + k_z^2}{2m} \]

Minimum energy included with a fixed number include all single particle states with \( k^2 < k^2_s \)

\[ E = 2 \int \frac{d^3k}{(2\pi)^3} \theta(k_x^2 + k_y^2 + k_z^2) \frac{k_x^2 + k_y^2 + k_z^2}{2m} \]

For spherical \( k_x^2 + k_y^2 + k_z^2 \) have no fixed

\[ E = \frac{2}{(2\pi)^3} \int \frac{d^3k}{(2\pi)^3} \frac{k_x^2}{2m} \left( \frac{k_x^2 + k_y^2 + k_z^2}{2m} \right) \]

\[ E = \frac{2}{(2\pi)^3} \int \frac{d^3k}{(2\pi)^3} \frac{k_x^2}{2m} \left( \frac{k_x^2 + k_y^2 + k_z^2}{2m} \right) \]

\[ E = \frac{2}{(2\pi)^3} \int \frac{d^3k}{(2\pi)^3} \frac{k_x^2}{2m} \left( \frac{k_x^2 + k_y^2 + k_z^2}{2m} \right) \]

\[ E = \frac{2}{(2\pi)^3} \int \frac{d^3k}{(2\pi)^3} \frac{k_x^2}{2m} \left( \frac{k_x^2 + k_y^2 + k_z^2}{2m} \right) \]

\[ E = \frac{2}{(2\pi)^3} \int \frac{d^3k}{(2\pi)^3} \frac{k_x^2}{2m} \left( \frac{k_x^2 + k_y^2 + k_z^2}{2m} \right) \]

\[ E = \frac{2}{(2\pi)^3} \int \frac{d^3k}{(2\pi)^3} \frac{k_x^2}{2m} \left( \frac{k_x^2 + k_y^2 + k_z^2}{2m} \right) \]

\[ E = \frac{2}{(2\pi)^3} \int \frac{d^3k}{(2\pi)^3} \frac{k_x^2}{2m} \left( \frac{k_x^2 + k_y^2 + k_z^2}{2m} \right) \]
total particle number

\[ N = \frac{2}{\pi^2} \int_0^{k_F} \frac{\omega}{\pi} \, d\omega \]

some is \( E \) calculation without \( \frac{e^2 k_o^2}{\omega} \)
so do some steps

\[ \frac{L^3}{\pi^2} \int_0^{k_F} \omega \, d\omega = \frac{L^3 k_F^5}{3 \pi^2} \]

more use \( f_+ \)

\[ E = \frac{\omega}{v_0} = \frac{k_F^5}{\omega \pi^2 \omega} \]

\[ p_{-0} = \frac{N}{v_0} = \frac{k_F^4}{2 \pi^2} \quad \text{or} \quad k_F = \left( \frac{3 \pi^2 \omega}{\hbar} \right)^{1/5} \]

so \( \omega = \frac{3 \pi^2 \pi^{4/5} \omega^{1/5} E^{1/5}}{10 \pi} \)

now in theroed

\[ P = -\frac{dE}{\partial V} \bigg|_N \quad \text{analog to} \quad F = -\nabla V \]

\[ E = \left( \frac{3 \pi^2 \pi^{4/5}}{10 \pi} \right) \omega^{3/5} \frac{\omega}{\omega^{1/5}} \left( \frac{3 \pi^2 \pi^{4/5}}{10 \pi} \right)^{1/5} \omega^{1/5} \omega^{2/5} \omega^{3/5} \]

\[ \frac{\partial E}{\partial V} \bigg|_N = \left( \frac{3 \pi^2 \pi^{4/5}}{10 \pi} \right) N^{5/3} \left( \frac{1}{3} \right) \omega^{5/3} - \frac{1}{3} \left( \frac{3 \pi^2 \pi^{4/5}}{10 \pi} \right)^{2/5} \omega^{1/5} \omega^{2/5} \omega^{3/5} \]

this is the "degeneracy pressure"
Less spherical Cow approx for electrons in metal

- electron-electron interactions neglected
- electrons interact with a periodic potential due to crystal with nuclei & bound electrons

1st consider 1-particle in periodic potential; for applied simplicity 1st do 1 dimension

\[ V(x+q) = V(x) \quad \text{periodicity} \]

\[ \hat{H} = \frac{\hbar^2}{2m} \Delta^2 + V(x) \]

Does periodicity tell us anything about spectra?

Yes! Intuitive argument: \( \psi(x+q) = e^{iq\phi(x)} \psi(x) \)

Define a finite translation operator

\[ \hat{D} |x> = |x+q> \]

Now it is easy to see that \( \hat{D} \) is unitary.
\( |\psi\rangle = \int dx \ 1 \langle x | \psi \rangle = \int dx \ 1 \langle x | \psi \rangle \Psi(x) \)

so \( \hat{O} |\psi\rangle = \int dx \ \hat{O}(x) \langle x | \psi \rangle = \int dx \ \hat{O}(x-a) \Psi(x) \) but \( x \) is dummy.

Let \( y = x-a \), \( x = y+q \)

\( = \int dy \ \hat{O} \Psi(y+q) \)

\( = \int dx \ \Psi(x-q) \)

so \( \langle \psi | \hat{O}^+ = (\hat{O}(\psi) \rangle = \int dx \ \Psi^*(x+q) \langle x \rangle \)

\( \langle \psi | \hat{O}^+ \hat{O} \langle \psi \rangle \rangle = \int dx \ \Psi^*(x+q) \Psi(x+q) \)

\( = \int dx \ \Psi^*(x+q) \Psi(x+q) \) let \( y = x+q \)

\( = \int dy \ \Psi^*(y) \Psi(y) = 1 \)

\( \Rightarrow \hat{O}^+ \hat{O} = 1 \) since this true for all \( |\psi\rangle \)

therefore \( \hat{O} \) is unitary

Now principal claim

\[ [0, \hat{A}] = 0 \]
Proof: several steps

Claim \[ \hat{D}^+ \hat{x} \hat{D} = x + a \]

proof
\[ \hat{D}^+ \hat{x} \hat{D} \mid x \rangle \langle x + a \rangle = \hat{D}^+ \langle x + a \rangle \langle x \rangle = (x + a) \hat{D}^+ \langle x + a \rangle \langle x \rangle \]

but the operator which has \( x \) as eigenstate \( \langle x \rangle \) with eigenvalue \( x \) is \( x \hat{a} \hat{x} = x \cdot \hat{a} \cdot x = a \cdot x \)

Claim \[ \hat{D}^+ \hat{x}^n \hat{D} = \bigcirc (x + a)^n \]

proof
\[ \hat{D}^+ \hat{x}^n \hat{D} = \hat{D}^+ \hat{x}^{n-1} \hat{x} \hat{D} \]

\[ \hat{D}^+ \hat{D} = \sum_{n=0}^{\infty} \frac{\hbar^2}{2m} \hat{x}^n \hat{D} \hat{x}^n \]

\[ \hat{D}^+ \hat{D} = \sum_{n=0}^{\infty} \frac{\hbar^2}{2m} \hat{x}^n \hat{D} \hat{x}^n \]

Claim \[ \hat{D}^+ f(x) \hat{D} = f(x + a) \]

proof expand \( f(x) \) is \( n \) Taylor Series \[ f(x) = \sum_{n=0}^{\infty} \frac{f^{(n)}(x)}{n!} x^n \]

\[ \hat{D}^+ f(x) \hat{D} = \sum_{n=0}^{\infty} \frac{f^{(n)}(x)}{n!} \hat{D} \hat{x}^n \hat{D} = \sum_{n=0}^{\infty} \frac{f^{(n)}(x)}{n!} (x + a)^n = f(x + a) \]

So consider

\[ \hat{D}^+ \hat{A} \hat{D} \]

with a periodic potential \( V(x + a) = V(x) \)

\[ \hat{D}^+ \hat{A} \hat{D} = \hat{D}^+ \hat{A} \hat{D} + \hat{D}^+ \hat{V}(x) \hat{D} \]

\[ \hat{D}^+ \hat{V}(x) \hat{D} = V(x + a) \]

\[ \hat{D}^+ \hat{V}(x) \hat{D} = V(x) \]
Now consider \( \langle \psi | 0^+ \frac{\hat{p}^2}{2m} 0 | \psi \rangle \)

\[
= \int dx \, \psi^* (x + \alpha) \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi (x + \alpha)
\]

Let \( y = x + \alpha \)

\[
= \int dy \, \psi^* (y) \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial y^2} \psi (y)
\]

\[
= \langle \psi | \frac{-\hbar^2}{2m} \hat{p}^2 | \psi \rangle
\]

true for all \( | \psi \rangle \) so

\[
\frac{\hbar^2}{2m} \hat{\mathbf{p}}^2 \hat{\mathbf{p}}^2 0 = \frac{\hbar^2}{2m} \hat{\mathbf{p}}^2
\]

or

\[
\hat{\mathbf{p}}^2 \hat{\mathbf{p}}^2 0 = \hat{\mathbf{p}}^2
\]

\[
\hat{\mathbf{p}}^2 0 = 0 \hat{\mathbf{p}}^2
\]

\[
0 \hat{\mathbf{p}}^2 0 = 0
\]

\[
[\hat{\mathbf{p}}, \hat{\mathbf{p}}^2] = 0
\]
Now \([H, \hat{D}] = 0\) so eigen vectors of \(H\) are

simultaneously eigen vectors of \(\hat{D}\) (if \(H\) has degeneracy we can always arrange this; otherwise automatic)

Now \(\hat{D}\) is unitary and thus has eigenvalues which are pure phases

First, diagonalize \(\hat{D}\) get \(\left( \begin{array}{cc} \lambda_n & 0 \\ 0 & \lambda_n \end{array} \right) \) where \(\lambda_n\) is eigenvalue

Diagonalize \(\hat{D}^*\) get \(\left( \begin{array}{cc} \lambda_n & 0 \\ 0 & \lambda_n \end{array} \right) \)

so \(\hat{D}^* \hat{D} = \left( \begin{array}{cc} \lambda_n^2 & 0 \\ 0 & \lambda_n^2 \end{array} \right) \)

so \(\hat{D}^* \hat{D} = \mathbb{1}\) or \(\lambda_n = \pm 1\)

All eigenvalues of \(\hat{D}\) are phases

Suppose \(|\psi_n\rangle\) is an eigen state of \(\hat{D}\)

it is also an eigenstate of \(\hat{D}\)

\(\hat{D} |\psi_n\rangle = e^{i \phi_n} |\psi_n\rangle\)

so \(\langle x | \hat{D} |\psi_n\rangle = \psi_n(x + a)\)

but \(\langle x | \hat{D} |\psi_n\rangle \leq e^{\phi_n} \langle x | \psi_n \rangle = e^{i \phi_n} \psi_n(x)\)

so \(\psi_n(x + a) = e^{i \phi_n} \psi_n(x)\)

Note \(\psi_n(x + 2a) = e^{i \phi_n} \psi_n(x)\)

\(\psi_n(x + \lambda_n a) = e^{i \phi_n} \psi_n(x)\)
Cute way to write this

if \( \psi(x) \) is an eigenstate of \( H \) then

\[
\psi(x) = e^{ikx} u(x) \quad \text{where} \quad u(x+q) = u(x)
\]

Bloch's theorem,

\[
\psi(x+q) = e^{ikq} e^{ikx} u(x+q) = e^{ikq} \psi(x)
\]

call \( \phi = kq \) and this is previous form

\( kq \) is called the crystal momentum

- \( k \) is continuous, not like is confined in
  wave function not normalized
  \[-\frac{\pi}{a} < k < \frac{\pi}{a} \quad \text{(then it repeats)}\]

- this cannot be all info (plane waves have no way to fix \( k \) in a finite bond)
  so eigen vectors have two labels
  \( \lambda \), where \( \lambda \) is discrete
  and \( k \) continuous
etc.

Note my picture has gaps

E cannot take all values

Let us do an example to see how this works

Kronig - Penney model

\[ V(x) = -\frac{e^2}{\epsilon} \sum_j \delta(x - j a) \]
periodically placed S (attractive)

toy model but illustrates point

for \( x \) not at \( S \) function

\[
-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E \psi \quad \Rightarrow \quad k = \frac{\sqrt{2mE}}{\hbar}
\]

or

\[
\frac{\partial^2 \psi}{\partial x^2} = -k^2 \psi
\]

\[
\psi(x) = A \sin(kx) + B \cos(kx) \quad \text{for} \quad 0 < x < \frac{\pi}{k}
\]

\[
\psi(x - a) = e^{-ikx} \psi(x) \quad \text{for} \quad -a < x < 0
\]

\[
\psi(x) = e^{-ik} \psi(x + a) = e^{-ik} \left[ A \sin(kx) + B \cos(kx) \right]
\]

at \( x = 0 \) function cont.

\[
B = e^{ik} \left[ A \sin(ka) + B \cos(ka) \right]
\]

integrate both sides of Schrödinger eq.

\[
\int \left( -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} - E \psi \right) dx = 0
\]

\[
-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} - E \right) = \alpha \psi(x)
\]
so \[ \Psi'_+ - \Psi'_- = \frac{2\hbar}{\pi} \Psi(0) \]

\[ \frac{1}{2} A - e^{i \frac{3}{2} \hbar} - \frac{3}{2} \left[ A \cos(\frac{3}{2} \hbar) - B \sin(\frac{3}{2} \hbar) \right] = \frac{-2\pi}{\hbar^2} \frac{\hbar}{2} B \]

\[ \cos \left( \frac{3}{2} \hbar \right) = \cos \left( \frac{3}{2} \hbar \right) - \frac{\pi}{\hbar^2} \sin \left( \frac{3}{2} \hbar \right) \]

LHS bounded \[-1 < \cos \left( \frac{3}{2} \hbar \right) < 1 \]

this bound prevents solutions for some \( \theta \)'s (i.e. some \( \xi \)'s) giving gaps.

Study RHS near \( \hbar \theta = \pi \)

\[ \cos(\hbar \theta) = (-1)^n + \Theta(\hbar^2 \theta - n \pi)^2) \]

Taylor,

\[ \sin(\hbar \theta) = (-1)^n \left( \hbar \theta - n \pi \right) + \Theta(\hbar^2 \theta - n \pi)^2) \]

\[ \frac{\sin(\hbar \theta)}{\pi \hbar} = (-1)^n \left( \frac{\hbar \theta}{n \pi} - 1 \right) + \Theta(\hbar^2 \theta - n \pi)^2) \]

\[ = (-1)^n \left( \frac{\hbar \theta}{n \pi} - 1 \right) + \Theta(\hbar^2 \theta - n \pi)^2) \]
\[ \text{rhs} = (-1)^n \left[ 1 + 4 \frac{m^2}{k^2} \left( 1 - \frac{x^2}{m^2} \right) + \theta (\lambda x - \eta)^2 \right] \]

\[ \triangleright 0 \]

so near l.e.s.s.t. \[ |\text{rhs}| > 1 \]

but \[ |\text{l.h.s.}| < 1 \] so no solution.
Conductors & insulators

If $E_F$ (the Fermi energy) lies within a band, the you read it essentially as energy to excite an electron from ground state conductor.

If $E_F$ is at band gap insulator.
Part theory - 

Suppose \[ H = H_0 + H' \]

where we know how to find eigenvectors and eigenvalues of \( H_0 \) and \( H' \) is "small".

We want a method to approximately find eigenvector and eigenvalues of \( H \). Method should be systematic (get better as we work harder) and converge on exact answer. Example spin effects in hydrogen atom.

Method: perturbation theory

Condition \( H' \) is "small" - what does this mean?

We shall see later. Here just assume "small".

\[ H = H_0 + H' \]

\( d \) is a smallness parameter. We will keep it to keep track of orders of smallness and then set to unity it and

Since \( d \) multiplies \( H' \) and \( H' \) is small, anything proportional to \( d \sim H'^2 \) and is very small etc.
work in the eigenbasis of \( \hat{H}_0 \); this is the problem we know.

\[ \hat{H}_0 (\psi_\alpha^{(0)}) = E_\alpha^{(0)} \psi_\alpha^{(0)} \]  
\[ \langle \psi_\alpha^{(0)} | \psi_\alpha^{(1)} \rangle = \delta_{\alpha \alpha} \]

we want to solve \( \hat{H}|\psi_\alpha\rangle = E_\alpha |\psi_\alpha\rangle \) \( \hat{H} = \hat{H}_0 + \hat{H}' \)

trick write everything as a Taylor series in \( \lambda \) with \( \alpha \) very small

\[ |\psi_\alpha\rangle = |\psi_\alpha^{(0)}\rangle + \lambda (|\psi_\alpha^{(1)}\rangle + \lambda^2 |\psi_\alpha^{(2)}\rangle + \ldots) \]

\[ E_\alpha = E_\alpha^{(0)} + \lambda E_\alpha^{(1)} + \lambda^2 E_\alpha^{(2)} + \ldots \]

\[ \hat{H} = \hat{H}_0 + \lambda \hat{H}' \]

plug in

\[ (\hat{H}_0 + \lambda \hat{H}') (|\psi_\alpha^{(0)}\rangle + \lambda (|\psi_\alpha^{(1)}\rangle + \lambda^2 |\psi_\alpha^{(2)}\rangle + \ldots)) = \]

\[ (E_\alpha^{(0)} + \lambda E_\alpha^{(1)} + \lambda^2 E_\alpha^{(2)} + \ldots) (|\psi_\alpha^{(0)}\rangle + \lambda (|\psi_\alpha^{(1)}\rangle + \lambda^2 |\psi_\alpha^{(2)}\rangle + \ldots)) \]

equate powers of \( \lambda \); since \( \alpha \) holds for all \( \lambda \) should hold order by order

\[ \hat{H}_0 |\psi_\alpha^{(0)}\rangle + \lambda (\hat{H}_0 |\psi_\alpha^{(0)}\rangle + H_0 |\psi_\alpha^{(1)}\rangle) + \lambda^2 (\hat{H}_0 |\psi_\alpha^{(0)}\rangle + H_0 |\psi_\alpha^{(1)}\rangle + \hat{H}_0 |\psi_\alpha^{(2)}\rangle + \ldots) = \]

\[ = E_\alpha^{(0)} |\psi_\alpha^{(0)}\rangle + \lambda (E_\alpha^{(1)} |\psi_\alpha^{(0)}\rangle + E_\alpha^{(2)} |\psi_\alpha^{(1)}\rangle + \ldots) + \lambda^2 (E_\alpha^{(1)} |\psi_\alpha^{(0)}\rangle + E_\alpha^{(1)} |\psi_\alpha^{(1)}\rangle + \ldots) + \ldots \]
\[ H_0 \psi_n^{(0)} = E_n \psi_n^{(0)} \]

\[ H' \psi_n^{(0)} + H_0 \psi_n^{(0)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(2)} \psi_n^{(0)} \]

\[ N' \psi_n^{(0)} + H_0 \psi_n^{(0)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(2)} \psi_n^{(0)} + \cdots \]

\[ H \psi_n = \psi_n^{(0)} + \psi_n^{(1)} + \psi_n^{(2)} + \cdots \]

Equation \( i \) is trivially true.

Equation \( ii \) gives

\[ \langle \psi_n^{(0)} | H' \psi_n^{(0)} + H_0 \psi_n^{(0)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(2)} \psi_n^{(0)} \]
\[ E_n^{(2)} = \langle \psi_0^{(2)} | H | \psi_0^{(1)} \rangle \]

Shift in energy is just expectation value of the shift in \( H \) in the old state.

What about \( | \psi_0^{(1)} \rangle \)?

\[ | \psi_0^{(1)} \rangle = \sum_n c_{nn} | \psi_n \rangle \quad \text{our job is to find } c_{nn} \]

Chain \( c_{nn} = 0 \) proof

\[ 1 = \langle \psi_n | \psi_n \rangle \quad \text{but} \quad | \psi_0 \rangle = | \psi_0^{(0)} \rangle + \lambda | \psi_0^{(1)} \rangle + O(\lambda^2) \]

\[ 1 = \langle \psi_0^{(0)} | \psi_0^{(0)} \rangle + \lambda \langle \psi_0^{(0)} | \psi_0^{(1)} \rangle + \lambda \langle \psi_0^{(1)} | \psi_0^{(1)} \rangle + O(\lambda^2) \]

\[ = \langle \psi_0^{(0)} | \psi_0^{(0)} \rangle + \lambda (\langle \psi_0^{(0)} | \psi_0^{(1)} \rangle + \langle \psi_0^{(1)} | \psi_0^{(1)} \rangle) + O(\lambda^2) \]

\[ = \langle \psi_0^{(0)} | \psi_0^{(0)} \rangle - \lambda^2 = 0 \]

so \( | \psi_0^{(1)} \rangle \) is orthogonal to \( | \psi_0^{(0)} \rangle \) \( c_{nn} = 0 \)

To find \( c_{nn} \), take ii) and right multiply by \( | \psi_n \rangle \)

\[ c_{nn} = \langle \psi_0^{(0)} | \psi_n \rangle \]

but ii) gives
\[ \langle \psi_n^{(0)} | H | \psi_n^{(0)} \rangle = \langle \psi_n^{(0)} | H_0 | \psi_n^{(0)} \rangle + \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle = E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle \]

or \[ \langle \psi_n^{(0)} | H | \psi_n^{(0)} \rangle = (E_n^{(0)} - E_m^{(0)}) \langle \psi_m^{(0)} | \psi_n^{(0)} \rangle \]

\[ = (E_n^{(0)} - E_m^{(0)}) C_{mn} \]

so \[ C_{mn} = \frac{\langle \psi_m^{(0)} | H | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \]

\[ |\psi_n^{(0)}\rangle = \sum_m C_{mn} |\psi_m^{(0)}\rangle \]

\[ |\psi_m^{(0)}\rangle = \sum_{m'} E_{m'}^{(0)} \frac{\langle \psi_m^{(0)} | H | \psi_{m'}^{(0)} \rangle}{E_{m'}^{(0)} - E_{m}^{(0)}} \]

Let us return to question of how small \( E' \) must be.

Claim \[ \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle < 1 \]

for all relevant \( n, l \)
Finally, let's look at $E^{(2)}$

take eq. (iii) and let mult by $\langle \psi_n^{(0)} |$

$$\langle \psi_n^{(0)} | H_0 | \psi_n^{(0)} \rangle + \frac{\langle \psi_n^{(0)} | H_0 | \psi_n^{(0)} \rangle}{E_n^{(2)}} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle =$$

$$E_n^{(2)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + E_n^{(1)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle + E_n^{(0)} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$$

so

$$E_n^{(2)} = \langle \psi_n^{(0)} | H_0 | \psi_n^{(0)} \rangle$$

$$= \langle \psi_n^{(0)} | H_0 \Sigma_{m+n} \frac{E_n - E_m}{E_n - E_m} \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$$

$$= \Sigma_{m+n} \frac{E_n - E_m}{E_n - E_m} \langle \psi_n^{(0)} | H_0 | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle$$

Note for ground state

$$E_n^{(2)} < 0 \quad \text{since} \quad E_n > E_0$$

Higher order calculations possible but get too long?
Summary:

\[ H = H_0 + H' \]

\[ E_n = E_n^{(0)} + \langle \psi_n | H | \psi_n^{(0)} \rangle + \sum \frac{\langle \psi_n | H_m^{(0)} | \psi_n^{(0)} \rangle}{E_n - E_m} + O(\lambda^2) \]

\[ |\psi_n^G\rangle = |\psi_n^{(0)}\rangle + \frac{\lambda}{E_n - E_m} \sum |\psi_n^{(0)} \times |\psi_n^{(0)}\rangle |\psi_n^{(0)}\rangle + O(\lambda^2) \]

Examples:
Suppose I put a "small" function of strength \( \lambda \) in middle of H.O.

\[ H = \frac{\hat{p}^2}{2m} + \frac{\lambda}{\beta} \hat{x}^2 + \lambda \phi(x) \]

\[ H_0 = \hat{p}^2/2m + \frac{\lambda}{\beta} \hat{x}^2 \]

What is ground state Energy

\[ E_n^{(0)} = \frac{\hbar^2}{2m} \]

\[ E_n^{(0)} = \langle \hat{H}_0 | \psi_n^{(0)} \rangle = \alpha \int dx \psi_n^{(0)}(x) \psi_n^{(0)}(x) = \alpha \psi_n^{(0)}(0) \psi_n^{(0)}(0) \]

\[ \psi_n^{(0)}(x) = \left( \frac{m \lambda}{\pi \hbar^2} \right)^{1/4} e^{-\frac{m \lambda x^2}{2 \hbar^2}} \]
so \( E_n = \frac{\hbar}{\sin \theta} \left( \frac{m \omega}{\hbar} \right)^{\frac{1}{2}} \)

or

\[ E \approx E_0 + \alpha \left( \frac{m \omega}{\hbar} \right)^{\frac{1}{2}} + \cdots \]

what about second order?

\[
E^{(2)}_0 = \left\langle \left| H' \right|^2 / 2 \right\rangle
\]

\[
E_0 - E_0^{(2)} = -n^2 \hbar \omega
\]

\[
\left( \phi_n^{(0)} \right)^* \left\langle H' \right| \phi_n^{(0)} \rangle = \int \phi_n^{(0)}^* \left( \phi_n^{(0)} \right) \phi_n^{(0)}^* \left( \phi_n^{(0)} \right) \phi_n^{(0)}^* \left( \phi_n^{(0)} \right)
\]

look up h.o. wave function

\[
\psi_n^{(0)}(x) = \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n \left( \frac{m \omega}{\hbar} x \right) e^{-x^2 / 2}
\]

so

\[
\psi_n^{(0)}(0) = \left( \frac{m \omega}{\pi \hbar} \right)^{\frac{1}{4}} \frac{1}{\sqrt{2^n n!}} H_n (0)
\]

Note \( H_n (0) = 0 \) for all odd \( n \)

\( H_0 (0) = 1, \ H_2 (0) = -2, \ H_4 (0) = 12 \)

\( n = 0 \)
\[ E_{12} = \sum_0^{\infty} \left( \frac{\pi}{\omega} \right)^2 \left( \frac{H_0(x)}{x^2} \right)^2 \frac{\omega^2}{2\hbar^2} \frac{n^2}{2^2} \]

\[ = -\frac{\alpha^2 \hbar}{\pi^2} \sum_1^{\infty} \left( \frac{H_0(x)}{x^2} \right)^2 \frac{n^2}{2^2} \]

\[ \mathbf{mathematica} \]

\[ x_68 \]

dimensions

clock

\[ E = \frac{\hbar}{2} + \alpha \frac{\hbar^2}{4\hbar^2} \frac{n^2m^2}{\hbar^2} - \alpha \frac{\hbar^2}{4\hbar^2} \frac{n^2m^2}{\hbar^2} \]

Note pattern

0th order easy
1st order more work
2nd order lots of work

work more and more to get less and less
Example:

Anharmonic oscillator

\[ H = \frac{1}{2} \hat{p}^2 + \frac{1}{2} k \hat{x}^2 + \alpha \hat{x}^4 \]

Grand state

\[ E_{0;0} = \frac{1}{2} \hbar \omega \]

\[ E^{(0)} = \langle \psi_{0;0} | \alpha \hat{x}^4 | \psi_{0;0} \rangle \]

\[ \hat{x}^4 = \frac{k^2}{\hbar^2 m^2 \omega^4} \]

\[ \hat{x}^4 = \frac{k^2}{\hbar^2 m^2 \omega^4} \left( \hat{p}^4 + 6 \hat{p}^2 \hat{x}^2 + 5 \hat{x}^4 \right) \]

Only terms with some number of \( \hat{p} \)'s or \( \hat{x} \)'s contribute

\[ \langle \psi_{0;0} | \hat{x}^4 | \psi_{0;0} \rangle = \frac{k^4}{\hbar^4 m^4 \omega^8} \left( 2 + 8 + 1 - 6 + 0 + 0 \right) \]

\[ = \frac{3 k^4}{4 \hbar^4 m^4 \omega^8} \]

So

\[ E = \frac{1}{2} \hbar \omega + \frac{3 \alpha k^2}{4 \hbar^2 m^2 \omega^2} \]
Example \[ V = \begin{cases} 3 \cos(\pi x) & x < 0 \\ 0 & x > 0 \end{cases} \]

so it is a square well with \( \cos \) perturbation.

\[ \hat{H}_3 \Psi_n(x) = E_n^{(0)} \Psi_n(x) \quad \Psi_n(x) = \frac{1}{\sqrt{L}} \sin\left(\frac{n\pi x}{L}\right) \quad \text{from } 0 < x < L \]

\[ H' = \pi \cos\left(\frac{\pi x}{L}\right) \]

\[ E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2 \]

\[ E_n^{(1)} = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \ldots \]

\[ E_n^{(1)} = \int_0^L dx \, \Psi_n^{(0)}(x) \, \pi \cos\left(\frac{\pi x}{L}\right) \Psi_n(x) \]

\[ = \int_0^L dx \, \frac{3 \pi}{4} \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right) \]

\[ = \int_0^L dx \, \frac{3 \pi}{4} \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) \]

\[ = \frac{9}{4} \int_0^L dx \, \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{\pi x}{L}\right) = 0 \]

\[ E_n^{(2)} = \frac{\mathcal{E}_{n}^{(2)}}{E_n^{(0)} - E_n^{(1)}} \]
Now \( \langle \Psi_1 | H' | \Psi_n \rangle \)

\[ = \frac{1}{L} \int_0^L dx \left( \frac{2}{L} \sin \left( \frac{m \pi x}{L} \right) \cos \left( \frac{n \pi x}{L} \right) \right) \sin \left( \frac{n \pi x}{L} \right) \]

\[ = \frac{2}{L} \int_0^L dx \sin \left( \frac{m \pi x}{L} \right) \sin \left( \frac{n \pi x}{L} \right) \]

\[ = \delta_{m,2} \left( \frac{9}{2} \right) \frac{L}{2} = \frac{9}{2} \delta_{m,2} \]

\[ E_{1(2)} = \frac{(\frac{9}{2})}{E_{100} - E_{g0}} = \frac{(\frac{9}{2})}{\frac{2}{mL^2} \frac{m^2}{(1-4)}} = \frac{-q^2 \alpha L^2}{2mL^2} \]

\[ E = \frac{x^2 \alpha^2}{2mL^2} - \frac{q^2 \alpha m L^2}{8 \pi^2 L^2} + \Theta (q^3) \]
Standard Pert. theory generally fails when there are degenerate states

( exception: degeneracy is due to symmetry and part. has one symmetry as H_n then \( \langle \Psi_n | H_n | \Psi_n \rangle = 0 \) for degenerate \( \Psi_n \))

Consider for simplicity two degenerate states \( \Psi_1, \Psi_2 \)

\[ H \Psi_1 = E_1 \Psi_1 \]
\[ H \Psi_2 = E_2 \Psi_2 \]

Note any linear superposition is also degenerate

\[ \Psi_o = \alpha \Psi_1 + \beta \Psi_2 \]

\[ H \Psi_o = E \Psi_o \]

Now claim \( H = H_o + V \) generally will not have degeneracy (if \( V \) has different symmetry)

Key point danger is due to terms which go like \( \langle \Psi_n | H | \Psi_o \rangle \) which diverge
trick: pick 2 linear combos of $|\Psi^{(0)}_+\rangle$ and $|\Psi^{(0)}_-\rangle$ as near states

call them $|\Psi^{(0)}_+\rangle$ bad notation I'll follow book

$|\Psi^{(0)}_+\rangle = \alpha |\Psi_+\rangle + \beta |\Psi_-\rangle \quad 1 = |\alpha|^2 + |\beta|^2$

$|\Psi^{(0)}_-\rangle = \alpha |\Psi_-\rangle + \beta |\Psi_+\rangle$

with

$\langle \Psi^{(0)}_+ | \Psi^{(0)}_+ \rangle = 0$

and with

$\langle \Psi^{(0)}_- | \Psi^{(0)}_- \rangle = 0$

these are "good" states

1st order pert works directly with good states

$E^{(0)}_\pm = \langle \Psi^{(0)}_\pm | H | \Psi^{(0)}_\pm \rangle$

so how do I find $|\Psi_\pm\rangle$ in 2x2 basis

answer $|\Psi_\pm\rangle$ are eigenvectors of $H$

note eigenvectors are orthogonal

so satisfies boxed conditions
In that case

$E^{(1)}_1$ are just the eigenvalues of $H'$ in the 2x2 space of degenerate levels.

Define:

$w_{0a} = \langle \psi^{(0)}_a | H' | \psi^{(0)}_a \rangle$

$w_{1a} = \langle \psi^{(0)}_a | H' | \psi^{(0)}_b \rangle$

$w_{0b} = \langle \psi^{(0)}_b | H' | \psi^{(0)}_a \rangle = w_{1a}$

$w_{1b} = \langle \psi^{(0)}_b | H' | \psi^{(0)}_b \rangle$

Eigenvalues:

\[
\begin{pmatrix}
\frac{w_{0a} - w_{1a}}{2} & w_{1a} - w_{1b} \\
\frac{w_{0a} - w_{0b}}{2} & \frac{w_{0b} + w_{1b}}{2}
\end{pmatrix}
\]

\[
\det \left( \begin{array}{cc}
\frac{w_{0a} - w_{1a}}{2} & w_{1a} - w_{1b} \\
\frac{w_{0a} - w_{0b}}{2} & \frac{w_{0b} + w_{1b}}{2}
\end{array} \right) = 0
\]

Generalization to more than two degenerate states: a single "good" linear combinator of eigenstates of $H'$ in a multi-state degenerate basis.

$E^{(1)}_1$ are then the eigenvalues.
Example - 2-d harmonic oscillator with perturbation

\[ H = \frac{1}{2} \left( x^2 + y^2 \right) + \frac{\beta}{2} x y \]

unperturbed eigenstates

\[ |n_x, n_y\rangle \quad H |n_x, n_y\rangle = \omega(n_x + n_y + 1) |n_x, n_y\rangle \]

note total energy = \( \hbar \omega (n + 1) \) \quad \( N = n_x + n_y \)

\( N \) is degenerate for \( N > 0 \)

\( N=1 \) \quad \( n_x = 1 \) also \( n_y = 0 \) or \( n_y = 0 \) also doubly

\( N=2 \) \quad \( n_x = 0 \) also \( n_y = 0 \) also \( n_x = 1 \) also \( n_y = 1 \) triple

etc.

Let's look at \( N = 1 \) states. What does perturbation do to them?

\[ |1, 0\rangle = 1, 0 \quad |1, 1\rangle = 0, 1 \quad \omega_{10} = \langle 1, 0 | \hat{H} | 1, 0 \rangle = \hbar \omega (1) \langle 1 | x y | 1 \rangle = 0 \]

\[ \omega_{00} = \text{similarly} \quad \omega_{11} \]

\[ \omega_{10} = \frac{1}{\hbar} \langle 1 | x y | 0 \rangle = \frac{1}{\hbar} \langle 1 | x y | 1 \rangle = \frac{1}{\hbar} | 1, 1 \rangle \]
\[ x = \sqrt{E_{\text{max}}} \quad (6+6') \]

so \( \langle 1| \hat{x}^2 | 0 \rangle = \frac{\hbar^2}{2m_0} \) \quad \langle 0 | \hat{y}^2 | 1 \rangle = \langle 1 | \hat{y}^2 | 0 \rangle \)

\[ \omega_{\text{conf}} = \frac{\hbar}{2m_0} \]

so \( \omega = \begin{pmatrix} 0 & \frac{\hbar}{2m_0} \\ \frac{\hbar}{2m_0} & 0 \end{pmatrix} \)

Eigenvalue \( E_{\pm} = \pm \frac{\hbar}{2m_0} \) easy to get

'good' eigen state \( \begin{pmatrix} \frac{\hbar}{m_0} \\ \frac{\hbar}{m_0} \end{pmatrix} \)

\( |k\rangle = \frac{1}{\sqrt{2}} |0\rangle + \frac{i}{\sqrt{2}} |1\rangle \quad |\kappa\rangle = \frac{1}{\sqrt{2}} |k\rangle - \frac{i}{\sqrt{2}} (\dagger \rangle \)
Example -

Fine structure of Hydrogen

\[ n = -\frac{\alpha^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r^2} \] 
was solved this

perturbations: many types

two largest "fine structure"

two types of effects here

- Relativity (splits states of same \( n \)
  and different \( l \))

- Sp. orb. (splits state of same \( \ell \)
  but different \( \ell = 0 + \frac{1}{2} \))
Lowest relativistic effect

\[ N = \frac{p^2}{2m} + V \]

but this is non-rel.

Relativistically:

\[ T = \sqrt{\frac{p^2}{m^2}} = \sqrt{\frac{p^2}{m^2} + mc^4} - mc^2 \]

\[ = mc^2 \left[ \sqrt{1 + \frac{p^2}{m^2}} - 1 \right] = \]

\[ = mc^2 \left( 1 + \frac{1}{2} \frac{p^2}{m^2} - \frac{1}{2} \frac{p^4}{m^4} + \cdots \right) \]

leading corr:

\[ = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} \]

\[ \text{treat as } H' \]

Claim: We can compute this using non-degenerate pert. theory in a bi-orthogonal basis

automatically diagonalized in this basis — why?
\[ E_{nlj}^{(0)} = \langle nlm | \hat{v} | nlm \rangle \]

there is a trick here

\[ \left( \frac{\hat{p}^2}{2m} + \hat{v} \right) |nlm\rangle = E_{nlj} |nlm\rangle \]

so

\[ \hat{p}^2 |nlm\rangle = \pm \hbar \Omega \left( 2m E_{nlj} - 2m \hat{v} \right) |nlm\rangle \]

\[ \hat{v}^2 |nlm\rangle = 4m \left( E_{nlj} - \nu \right)^2 |nlm\rangle \]

we know this

\[ \langle nlm | \hat{p}^2 | nlm \rangle = 4m \left( \frac{E_{nlj}^2}{2} + E_{nlj} \nu \langle nlm | \hat{v} | nlm \rangle + \langle nlm | \hat{v}^2 | nlm \rangle \right) \]

'simple matter to evaluate'

\[ E_{nlj}^{(0)} \quad \text{is known} \]

\[ \langle \nu \rangle = \frac{\left\langle \nu \right\rangle}{4 \pi\epsilon_0} \]

\[ \langle \nu^2 \rangle = \left( \frac{\left\langle \nu \right\rangle}{4 \pi\epsilon_0} \right)^2 \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(4\pi\epsilon_0)^2} \]
Combining fields

$$E'' = -\frac{E'}{2m_e c^2} \left[ \frac{4\pi}{k^2} - 2 \right]$$

Valid by itself for pionic atom

Proton is spin zero

Another effect of same size due to spin orbit

Claim

$$H' = \frac{i}{2} \left( \frac{e^2}{4\pi\varepsilon_0} \right) \frac{1}{m^2 c^4 r^3} \hat{L} \cdot \hat{S}$$

derivation:

- From Dirac equation in non-rel. seduction

best method

- Intuitive moving charge electron in proton's $E$ field gives $\mathbf{B}$ which interacts with $\mathbf{S}$

$$\mathbf{B} = \frac{\mathbf{\nabla} \times \mathbf{E}}{c^2}$$

1st non-rel. (See Purcell)
\[ E = \frac{Ze^2}{4\pi\varepsilon_0 r^2} \]

\[ |\psi| = \frac{L}{m^*} \]

So, as seen by electron

\[ B = \frac{Ze^2}{4\pi\varepsilon_0 m^* r^2} \]

Classical orbit

\[ M = 3 \left( \frac{s}{2m^*} \right) S = -\frac{Ze^2}{2m^*} \frac{s}{2m^*} = \frac{e^2}{8m^*} \]

Recall factor of 2 due to "g factor."

\[ H' = M \cdot B = \left( \frac{e^2}{4\pi\varepsilon_0} \right) \frac{1}{m^*} \frac{s}{2m^*} \]

Unfortunately, this is not right. There is an additional factor of \( \frac{1}{2} \) due to "Thomas precession."

Note: \( H' = -M \cdot B \) only is valid for an inertial frame but here electron is non-inertial. The derivation is subtle but gives \( \frac{1}{2} \)

\[ H' = \frac{1}{2} \left( \frac{e^2}{4\pi\varepsilon_0} \right) \frac{1}{m^*} \frac{1}{r^3} \frac{s}{2m^*} \]
Now again we have degenerate part. Hence need to choose "good" basis.

Claim $\ell^2$ is still good quantum number but $\ell_z$ is not good too but $m_\ell$ is not.

If $\ell \geq \frac{1}{2}$, $\ell_z$ does not commute with $L_z$ but does commute with $J^x, J^y, J^z$

$$J = L + \frac{1}{2}$$
$$L = \ell + \frac{1}{2}$$

$$E_{\ell \sigma} = \langle \ell \sigma \rangle = \frac{i}{2} \left( \frac{\hbar}{\mu \gamma_0} \right) \frac{1}{\hbar c^2} \left\langle \ell \sigma \langle \ell \sigma \langle \lambda \cdot \vec{S} \right| \frac{1}{r^3} \right\rangle$$

$$\langle \frac{1}{r^3} \rangle = \frac{1}{\epsilon_0} \frac{1}{\ell (\ell + \frac{1}{2}) (\ell + 1)}$$

$$\langle \ell \cdot \vec{S} \rangle = \frac{1}{2} \left( \frac{\vec{\ell}^2}{r^2} - \frac{\vec{\ell} \cdot \vec{S}}{r^2} \right)$$

-120 -