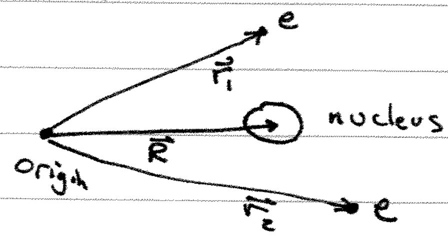
Approximate methods:

Consider Helium:



To solve this problem (i.e. find the energy levels & wavefunctions) we first need to write down the Hamiltonian.

$$\hat{H} = \hat{KE} + \hat{V}$$

There are 3 particles to worry about, and each has a kinetic energy:

$$\hat{KE} = \frac{-\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2$$

$\boxed{\text{Laplacian for nuclear coordinates}}$ $\boxed{\text{Laplacians for each set of electronic coordinates}}$

The potential also has 3 pair-wise terms:

$$\hat{V} = \frac{-2e^2}{4\pi\varepsilon_0|\vec{R}-\vec{r}_1|} - \frac{2e^2}{4\pi\varepsilon_0|\vec{R}-\vec{r}_2|} + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}$$

$$\hat{V} = V_{N-e_1} + V_{N-e_2} + V_{e_1-e_2}$$

This is a 3-body problem, which is, in general, unsolvable.

Approximation #: $M \gg m_e$, so we can treat the nucleus as <u>fixed</u> in space (at the origin). This is usually called the Born-Oppenheimer Approximation

$$\hat{H} = \frac{-\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}$$

The wavefunction is a function of both electron positions

$$\Psi = \Psi(\vec{r}_1, \vec{r}_2) = \Psi(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2)$$

The last term in the Hamiltonian is for inter-electron repulsion, and it makes even this simplified form unsolvable without approximation.
The first method we'll explore is the variational method

Variational method

Suppose we "forget" all we know about the Harmonic oscillator wavefunction. What would happen if we "guessed" a function: $\phi(x)$

What energy would we measure?

$$\langle E_\phi \rangle = \int_{-\infty}^{\infty} \phi(x)^* \hat{H} \phi(x)\, dx = \langle \phi | \hat{H} | \phi \rangle$$

(But what if ϕ wasn't normalized?)

$$\langle E_\phi \rangle = \frac{\int_{-\infty}^{\infty} \phi(x)^* \hat{H} \phi(x)\, dx}{\int_{-\infty}^{\infty} \phi(x)^* \phi(x)\, dx} = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle}$$

So what can we say about $\langle E_\phi \rangle$? Let's think about how we might figure out a value.

$$\phi(x) = \sum_{n=0}^{\infty} C_n \Psi_n(x)$$

$$|\phi\rangle = \sum_{n=0}^{\infty} C_n |n\rangle$$

we're just writing down $\phi(x)$ in terms of the real eigenfunctions of the H.O. (which we've forgotten)

Likewise

$$\phi(x)^* = \sum_{n=0}^{\infty} c_n^* \, \psi_n^*(x)$$

$$\langle \phi | = \sum_{n=0}^{\infty} c_n^* \langle n |$$

We can do the integrals after all:

$$\langle \phi | \phi \rangle = \left(\sum_{n=0}^{\infty} c_n^* \langle n | \right) \left(\sum_{n'=0}^{\infty} c_{n'} | n' \rangle \right)$$

$$= \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} c_n^* c_{n'} \underbrace{\langle n | n' \rangle}_{\int_{-\infty}^{\infty} \psi_n^*(x) \psi_{n'}(x) \, dx}$$

$$\delta_{n,n'}$$

$$= \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} c_n^* c_{n'} \underbrace{\delta_{n,n'}}_{\text{requires } n = n'}$$

$$= \sum_{n=0}^{\infty} c_n^* c_n = \sum_{n=0}^{\infty} |c_n|^2$$

What if we insert $\hat{H}$?

$$\int_{-\infty}^{\infty} \phi^*(x) \, \hat{H} \, \phi(x) \, dx = \langle \phi | \hat{H} | \phi \rangle$$

$$= \left(\sum_{n=0}^{\infty} c_n^* \langle n | \right) \hat{H} \left(\sum_{n'=0}^{\infty} c_{n'} | n' \rangle \right)$$

$$= \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} c_n^* c_{n'} \underbrace{\langle n | \hat{H} | n' \rangle}_{\int_{-\infty}^{\infty} \psi_n^*(x) \, \hat{H} \, \psi_{n'}(x) \, dx}$$

$$E_{n'} \, \delta_{n,n'}$$

$$= \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} c_n^* c_{n'} E_{n'} \underbrace{\delta_{n,n'}}_{\text{requires } n' = n}$$

$$= \sum_{n=0}^{\infty} |c_n|^2 E_n$$

OK, so:

$$\langle E_\phi \rangle = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\sum_{n=0}^{\infty} |c_n|^2 E_n}{\sum_{n=0}^{\infty} |c_n|^2}$$

What do we know about all the values of $E_1, \ldots E_\infty$?

They are <u>all</u> $\geq E_0$

$$\frac{\sum_{n=0}^{\infty} \left(|c_n|^2 E_n\right)}{\sum_{n=0}^{\infty} |c_n|^2} \geq \frac{\sum_{n=0}^{\infty} \left(|c_n|^2 E_0\right)}{\sum_{n=0}^{\infty} |c_n|^2} = \frac{\left(\sum_n |c_n|^2\right) E_0}{\sum_n |c_n|^2}$$

$\therefore$

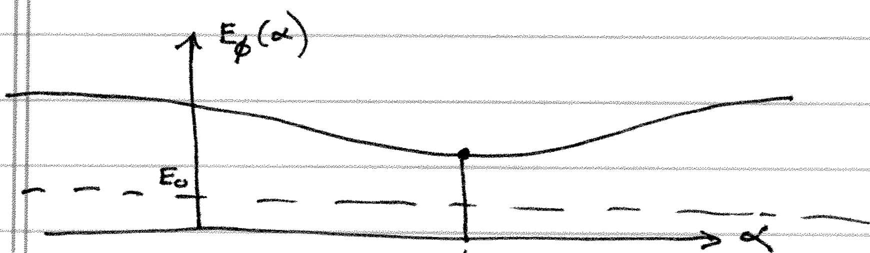
$$\boxed{\langle E_\phi \rangle \geq E_0}$$

$\leftarrow$ This is called the variational theorem

For <u>any</u> trial function $|\phi\rangle$, $E_\phi = \dfrac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \geq E_0$

How can we use this? We can make the trial function with a <u>parameter</u> $\phi(x\,;\alpha)$

function of x — parametrized by α



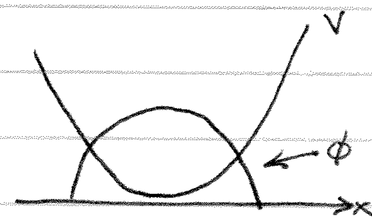
best value of α is lowest E_ϕ & closest to ground state energy.

<u>Example</u> $\hat{H} = \dfrac{-\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2$

$\psi_0 = ?$ $\leftarrow$ we forgot!

$\phi = \cos \lambda x \qquad \dfrac{-\pi}{2\lambda} \leq x \leq \dfrac{\pi}{2\lambda}$

variational parameter



$$\langle \phi | \hat{H} | \phi \rangle = \int_{-\pi/2\lambda}^{\pi/2\lambda} \cos(\lambda x) \left[\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{kx^2}{2} \right] \cos(\lambda x)\, dx$$

$$= \frac{\pi \hbar^2 \lambda}{4m} + \left(\frac{\pi^3}{48} - \frac{\pi}{8} \right) \frac{k}{\lambda^3}$$

$$\langle \phi | \phi \rangle = \int_{-\pi/2\lambda}^{\pi/2\lambda} \cos^2 \lambda x \, dx = \frac{\pi}{2\lambda}$$

$$\langle E_\phi \rangle = \frac{\hbar^2 \lambda^2}{2m} + \left(\frac{\pi^2}{24} - \frac{1}{4} \right) \frac{k}{\lambda^2}$$

Now what? How do we get the best λ? The lowest E_ϕ? Take $\frac{\partial E_\phi(\lambda)}{\partial \lambda} = 0$

So: $\frac{\hbar^2 \lambda}{m} + \left(\frac{\pi^2}{24} - \frac{1}{4} \right) \left(\frac{-2k}{\lambda^3} \right) = 0$

$$\lambda^2 = \sqrt{\frac{\pi^2}{24} - \frac{1}{4}} \sqrt{\frac{2km}{\hbar^2}} \longleftarrow$$ plug this back into E_ϕ

$$E_\phi = \left(\frac{\pi^2}{24} - \frac{1}{4} \right)^{1/2} \hbar\omega\sqrt{2}$$

$$E_\phi = 1.14 \frac{\hbar\omega}{2} \longleftarrow$$ not bad!

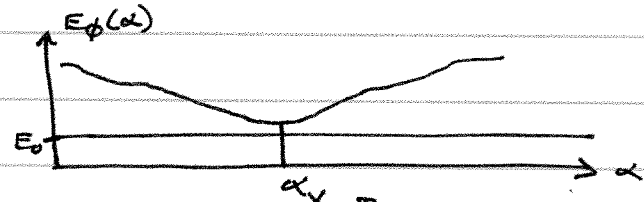
More on the Variational Method

This is an approximation method for unsolved problems.

$$\phi(\vec{r};\alpha) = \text{trial function of } \vec{r}\text{, \underline{parametrized} by } \alpha$$

$$E_\phi(\alpha) = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$$

Variational theorem: $E_\phi \geq E_0$ ← true ground state energy



← variational choice for α

Here's a real-world example: H-atom:

(radial only since $Y_0^0 = \frac{1}{\sqrt{4\pi}}$

$$\hat{H} = \frac{-\hbar^2}{2m_e r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$\phi(r;\alpha) = e^{-\alpha r^2}$$

What's the real one?

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$$\frac{\partial}{\partial r}\phi = -2\alpha r e^{-\alpha r^2}$$

$$r^2\frac{\partial}{\partial r}\phi = -2\alpha r^3 e^{-\alpha r^2}$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\phi\right) = \left(-6\alpha r^2 + 4\alpha^2 r^4\right)e^{-\alpha r^2}$$

$$\phi^* \hat{H}\phi = e^{-2\alpha r^2}\left(\frac{-m_e e^2 + 4\alpha\varepsilon_0\hbar^2\pi r(3-2\alpha r^2)}{4\varepsilon_0 m_e \pi r}\right)$$

$$E_\phi = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{4\pi\int_0^\infty r^2\,\phi^*\hat{H}\phi\,dr}{4\pi\int_0^\infty r^2\,\phi^*\phi\,dr}$$

$$= \frac{\dfrac{3\hbar^2\pi^{3/2}}{4\sqrt{2}\,m_e\,\alpha^{1/2}} - \dfrac{e^2}{4\varepsilon_0\,\alpha}}{\left(\pi/2\alpha\right)^{3/2}}$$

$$E_\phi = \frac{3\hbar^2\alpha}{2m_e} - \frac{e^2\alpha^{1/2}}{\sqrt{2}\,\varepsilon_0\,\pi^{3/2}}$$

Solving for α_v

$$\frac{dE_\phi}{d\alpha} = \frac{3\hbar^2}{2m_e} - \frac{e^2}{(2\pi)^{3/2}\,\varepsilon_0\sqrt{\alpha}} = 0$$

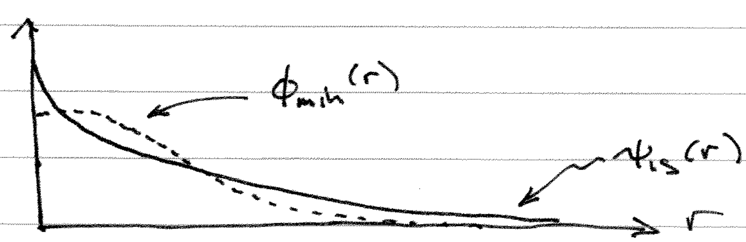
$$\alpha = \frac{m_e^2\,e^4}{18\,\pi^3\,\varepsilon_0^2\,\hbar^4} \longleftarrow$$ plug this back into E_ϕ to get E_{min}

$$E_{min} = \frac{-4}{3\pi}\left(\frac{m_e\,e^4}{16\,\pi^2\,\varepsilon_0^2\,\hbar^2}\right) = -0.424\ (\quad)$$

$$E_0 = -\frac{1}{2}\left(\frac{m_e\,e^4}{16\,\pi^2\,\varepsilon_0^2\,\hbar^2}\right) = -0.5\ (\quad)$$

$$\phi(\vec{r}) = \frac{8}{3^{3/2}\,\pi}\left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-(8/9\pi)\,r^2/a_0^2}$$

{ "Best" gaussian approximation to 1s



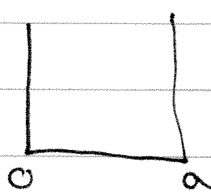
Can we do a better job? Throw more "stuff" into our trial function until it is perfect? Yes!

$$\phi(r) = \alpha e^{-ar^2} + \beta e^{-br^2} + \gamma e^{-cr^2} \qquad a \neq b \neq c$$

This is a 3-Gaussian (triple-zeta) approximation to $e^{-\alpha r}$. The variational parameters are α, β, and γ.

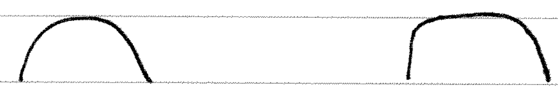
$E_\phi(\alpha, \beta, \gamma)$, so we need to find a good way to get E_ϕ minimized with respect to all 3 variables.

Another example:



$$\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

$$\phi(x; c_1, c_2) = c_1 \underbrace{x(a-x)}_{\text{parabola}} + c_2 \underbrace{x^2(a-x)^2}_{\text{quartic}}$$



In general $\phi = c_1 f_1 + c_2 f_2$

$$\phi = \sum_i \underbrace{c_i}_{\text{variational parameters}} \underbrace{f_i}_{\text{any functions we want!}}$$

What is E_ϕ?

$$\langle \phi | \hat{H} | \phi \rangle = \int (c_1 f_1 + c_2 f_2) \, \hat{H} \, (c_1 f_1 + c_2 f_2)$$

$$= c_1^2 \int f_1 \hat{H} f_1 + c_1 c_2 \int f_1 \hat{H} f_2 + c_2 c_1 \int f_2 \hat{H} f_1 + c_2^2 \int f_2 \hat{H} f_2$$

$$\langle \phi | \hat{H} | \phi \rangle = c_1^2 \langle f_1 | H | f_1 \rangle + c_1 c_2 \langle f_1 | \hat{H} | f_2 \rangle + c_2 c_1 \langle f_2 | \hat{H} | f_1 \rangle + c_2^2 \langle f_2 | \hat{H} | f_2 \rangle$$

$$= c_1^2 H_{11} + c_1 c_2 H_{12} + c_2 c_1 H_{21} + c_2^2 H_{22}$$

$$H_{ij} = \int f_i \hat{H} f_j \, d\vec{r}$$

Since $\hat{H}$ is hermitian, $\hat{H}_{ij} = \int f_i \hat{H} f_j = \int (H f_i)^* f_j$

$$= \int f_j \hat{H} f_i = \hat{H}_{ji}$$

Likewise $\langle \phi | \phi \rangle = \int (c_1 f_1 + c_2 f_2)(c_1 f_1^* + c_2 f_2)$

$$= c_1^2 \langle f_1 | f_1 \rangle + c_1 c_2 \langle f_1 | f_2 \rangle + c_2 c_1 \langle f_2 | f_1 \rangle + c_2^2 \langle f_2 | f_2 \rangle$$

$$= c_1^2 S_{11} + c_1 c_2 S_{12} + c_2 c_1 S_{21} + c_2^2 S_{22}$$

$$S_{ij} = \int f_i f_j \, d\vec{r} = S_{ji}$$

$$E_\phi (c_1, c_2) = \frac{c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 + 2 c_1 c_2 S_{12} + c_2^2 S_{22}}$$

We can rearrange this:

$$(c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22}) E_\phi = c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22}$$

Take <u>derivatives</u> of both sides with respect to c_1

$$(2 c_1 S_{11} + 2 c_2 S_{12}) E_\phi + (c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22}) \frac{\partial E_\phi}{\partial c_1} = 2 c_1 H_{11} + 2 c_2 H_{12}$$

When $\frac{\partial E}{\partial c_1} = 0$, were <u>at</u> the E_{min}, so:

$$(2c_1 S_{11} + 2c_2 S_{12})E = 2c_1 H_{11} + 2c_2 H_{12}$$

$$\boxed{c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0}$$

If we do the same for $\frac{\partial}{\partial c_2}$ and set $\frac{\partial E}{\partial c_2} = 0$

$$\boxed{c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0}$$

We can combine these into a determinant equation: to solve for E:

$$\begin{array}{cc} & \begin{array}{cc} \quad c_1 \quad & \quad\quad c_2 \quad \end{array} \\ \frac{\partial E}{\partial c_1} = 0 \Rightarrow & \\ \frac{\partial E}{\partial c_2} = 0 \Rightarrow & \end{array} \begin{vmatrix} (H_{11} - ES_{11}) & (H_{12} - ES_{12}) \\ (H_{12} - ES_{12}) & (H_{22} - ES_{22}) \end{vmatrix} = 0$$

"secular" determinant

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{12} - ES_{12})^2 = 0$$

quadratic "secular" equation for E

Variational Method using the Kitchen Sink

The basis:
$$E_\phi(\alpha) = \frac{\int \phi^* \hat{H} \phi}{\int \phi^* \phi}$$

$\phi(\vec{r};\alpha)$ is a trial function of $\vec{r}$, parameterized by α

We proved: $E_\phi(\alpha) \geq E_0 \leftarrow$ the true ground state

$$\frac{\partial E_\phi}{\partial \alpha} = 0 \leftarrow \text{finds extrema (minima \& maxima)}$$

Making better trial functions:

functional rep	Dirac representation	Matrix - Vector rep
$\phi = c_1 f_1 + c_2 f_2$	$\lvert\phi\rangle = c_1\lvert f_1\rangle + c_2\lvert f_2\rangle$	$\vec{\phi} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \begin{matrix} \leftarrow \text{"}f_1\text{" space} \\ \leftarrow \text{"}f_2\text{" space} \end{matrix}$
$H_{ij} = \int f_i^* \hat{H} f_j \, d\vec{r}$	$H_{ij} = \langle f_i \lvert \hat{H} \rvert f_j \rangle$	$\underline{\underline{H}} = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$
$S_{ij} = \int f_i^* f_j \, d\vec{r}$	$S_{ij} = \langle f_i \lvert f_j \rangle$	$\underline{\underline{S}} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}$

$$E_\phi = \frac{\int \phi^* H \phi \, d\vec{r}}{\int \phi^* \phi \, d\vec{r}} = \frac{\langle \phi \lvert \hat{H} \rvert \phi \rangle}{\langle \phi \lvert \phi \rangle} = \frac{\vec{\phi}^T \cdot \underline{\underline{H}} \cdot \vec{\phi}}{\vec{\phi}^T \cdot \underline{\underline{S}} \cdot \vec{\phi}}$$

"Schrodinger" "Dirac" "Heisenberg"

Last time:

$$E_\phi = \frac{\int (c_1 f_1^* + c_2 f_2^*) \hat{H} (c_1 f_1 + c_2 f_2) \, d\vec{r}}{\int (c_1 f_1^* + c_2 f_2^*)(c_1 f_1 + c_2 f_2) \, d\vec{r}}$$

$$= \frac{c_1^2 \int f_1^* \hat{H} f_1 + c_1 c_2 \int f_1^* \hat{H} f_2 + c_2 c_1 \int f_2^* \hat{H} f_1 + c_2^2 \int f_2^* \hat{H} f_2}{c_1^2 \int f_1^* f_1 + c_1 c_2 \int f_1^* f_2 + c_2 c_1 \int f_2^* f_1 + c_2^2 \int f_2^* f_2}$$

$$E_\phi = \frac{c_1^2 H_{11} + c_1 c_2 H_{12} + c_2 c_1 H_{21} + c_2^2 H_{22}}{c_1^2 S_{11} + c_1 c_2 S_{12} + c_2 c_1 S_{21} + c_2^2 S_{22}}$$

We'll use some symmetry $\quad H_{12} = H_{21}$

$S_{12} = S_{21}$

$$E_\phi(c_1, c_2) = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

We want <u>both</u> $\frac{\partial E}{\partial c_1} = 0$ <u>and</u> $\frac{\partial E}{\partial c_2} = 0$

Here's how we do it:

$$c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22} = E_\phi \left(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}\right)$$

Take derivative of both sides w.r.t. c_1

$$2c_1 H_{11} + 2c_2 H_{22} = \frac{\partial E_\phi}{\partial c_1}\left(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}\right) + E_\phi \left(2c_1 S_{11} + 2c_2 S_{12}\right)$$

this is $= 0$ at minimum, so:

$$2c_1 H_{11} + 2c_2 H_{12} = E_\phi \left(2c_1 S_{11} + 2c_2 S_{12}\right)$$

$$c_1 (H_{11} - E_\phi S_{11}) + c_2 (H_{12} - E_\phi S_{12}) = 0$$

Likewise for c_2: $\quad c_1 (H_{12} - E_\phi S_{12}) + c_2 (H_{22} - E_\phi S_{22}) = 0$

system of linear equations (2 eqns, 2 unknowns)

$$\begin{vmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} \\ H_{12} - E S_{12} & H_{22} - E S_{22} \end{vmatrix} = 0$$

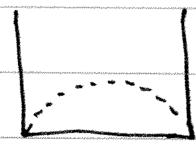
$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = 0$$

$$ad - bc = 0 \quad \leftarrow \text{Determinant of a } 2\times 2$$

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{12} - ES_{12})^2 = 0$$

⟸ Solve to get E!

Example:



0 a

$$\psi_0 = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} \qquad E_0 = ?$$

$$\phi = c_1 f_1 + c_2 f_2$$

$$f_1 = x(a-x) \qquad f_2 = x^2(a-x)^2$$

$$H_{11} = \int_0^a x(a-x) \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}\left(x(a-x)\right) dx = \frac{-\hbar^2}{2m} \int_0^a x(a-x) \frac{d^2}{dx^2}\left(ax - x^2\right) dx$$

$$= \frac{-\hbar^2}{2m} \int_0^a x(a-x) \frac{d}{dx}(a - 2x)\, dx = \frac{-\hbar^2}{2m} \int_0^a x(a-x)(-2)\, dx$$

$$= \frac{\hbar^2}{m} \int_0^a ax - x^2\, dx = \frac{\hbar^2}{m} \left[\frac{ax^2}{2} - \frac{x^3}{3}\right]_0^a$$

$$= \frac{\hbar^2}{m} \left[\frac{a^3}{2} - \frac{a^3}{3}\right] = \frac{a^3 \hbar^2}{6m}$$

$$H_{22} = \frac{a^3 \hbar^2}{105 m}$$

$$H_{12} = H_{21} = \frac{a^3 \hbar^2}{30 m}$$

$$S_{11} = \int_0^a x(a-x)\,x(a-x) = \int_0^a (xa-x^2)(xa-x^2)\,dx$$

$$= \int_0^a x^2a^2 - 2x^3a + x^4\,dx$$

$$= \left[\frac{x^3a^2}{3} - \frac{2x^4a}{4} + \frac{x^5}{5}\right]_0^a$$

$$= \frac{a^5}{3} - \frac{2a^5}{4} + \frac{a^5}{5}$$

$$= \frac{a^5}{30}$$

$$S_{22} = \frac{a^5}{630}$$

$$S_{12} = S_{21} = \frac{a^5}{140}$$

Putting it all together:

$$\begin{vmatrix} \frac{a^3\hbar^2}{6m} - E\frac{a^5}{30} & \frac{a^3\hbar^2}{30m} - E\frac{a^5}{140} \\ \frac{a^3\hbar^2}{30m} - E\frac{a^5}{140} & \frac{a^3\hbar^2}{105} - E\frac{a^5}{630} \end{vmatrix} = 0$$

Let $E' = E\frac{a^2m}{\hbar^2} \Rightarrow E = \frac{E'\hbar^2}{a^2m}$

$$\begin{vmatrix} \frac{a^3\hbar^2}{6m} - \frac{E'\hbar^2a^3}{30m} & \frac{a^3\hbar^2}{30m} - \frac{E'\hbar^2a^3}{140m} \\ \frac{a^3\hbar^2}{30m} - \frac{E'\hbar^2a^3}{140m} & \frac{a^3\hbar^2}{105} - \frac{E'\hbar^2a^3}{630m} \end{vmatrix} = 0$$

$$\frac{a^3\hbar^2}{m}\begin{vmatrix} \frac{1}{6} - \frac{E'}{30} & \frac{1}{30} - \frac{E'}{140} \\ \frac{1}{30} - \frac{E'}{140} & \frac{1}{105} - \frac{E'}{630} \end{vmatrix} = 0$$

$$\left(\frac{1}{6} - \frac{E'}{30}\right)\left(\frac{1}{105} - \frac{E'}{630}\right) - \left(\frac{1}{30} - \frac{E'}{140}\right)^2 = 0$$

$$(E')^2 - 56E' + 252 = 0$$

$$E' = \frac{56 \pm \sqrt{2128}}{2}$$

$$E' = 51.065 \quad \text{and} \quad 4.93487$$

$$E_{min} = 4.9347 \frac{\hbar^2}{a^2 m} = 0.125002 \frac{h^2}{a^2 m}$$

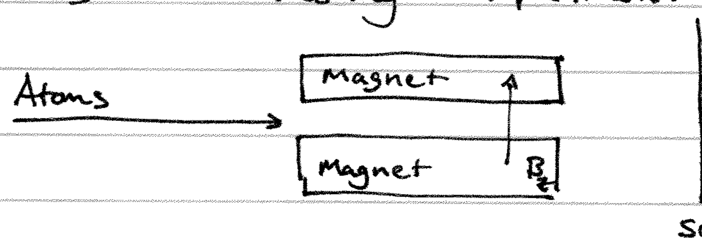
$$E_0 = \frac{h^2 n^2}{8ma^2} = \frac{1}{2}\frac{h^2}{ma^2} = 0.125 \frac{h^2}{a^2 m^2}$$

Spin

In the last 2 problems of the previous problem set, you showed that a magnetic field can have an effect on the energies and the size of that effect depends on the m quantum number:

$$E = \frac{-me^4}{8\varepsilon_0 h^2 n^2} + \beta_B m B_z \qquad \begin{matrix} n = 1, 2, 3 \ldots \\ m = 0, \pm 1, \pm 2 \ldots \end{matrix}$$

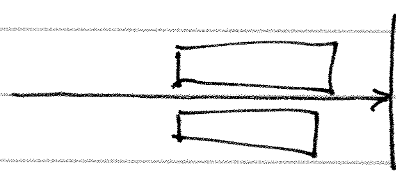
Here's an interesting experiment



In an inhomogeneous (changing) B field, we'd expect the atoms to move toward the direction that lowers their energies.

If $l = 0$ (i.e. s orbitals) what would we expect to see?

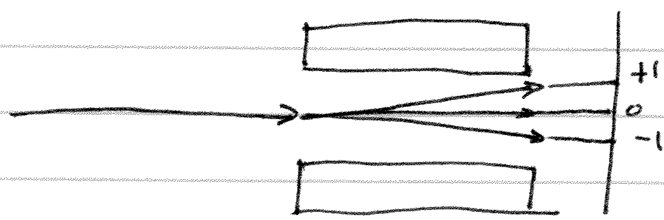
If $l = 0$, $m = 0$ also, so the field should do nothing!



one spot should appear on the screen.

If $l = 1$ (i.e. p orbitals occupied) what would we expect to see?

If $l = 1$, $m = -1, 0, +1$

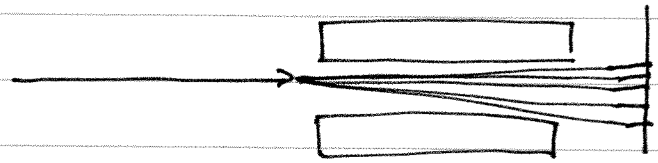


3 spot on screen

$n_{spots} = 2l + 1$

If $l=2$ (i.e. d orbitals occupied)

$m = -2, -1, 0, 1, 2$

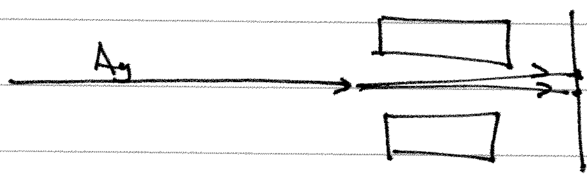


← 5 spots for $l=2$

That is $n_{spots} = 2l+1$ or $l = \frac{n_{spots} - 1}{2}$

A very famous experiment called the Stern-Gerlach experiment was trying to resolve the half-fill d-orbital rule e.g. $5s^2\ 4d^9 \rightarrow 5s^1\ 4d^{10}$ is the last electron in an s orbital (1 spot) or d orbital (5 spots)? What would you expect to see? How many spots?

Here's what they did see:



← 2 spots?

2 SPOTS!!!

So what is l?

$$l = \frac{n_{spots} - 1}{2} = \frac{1}{2}$$

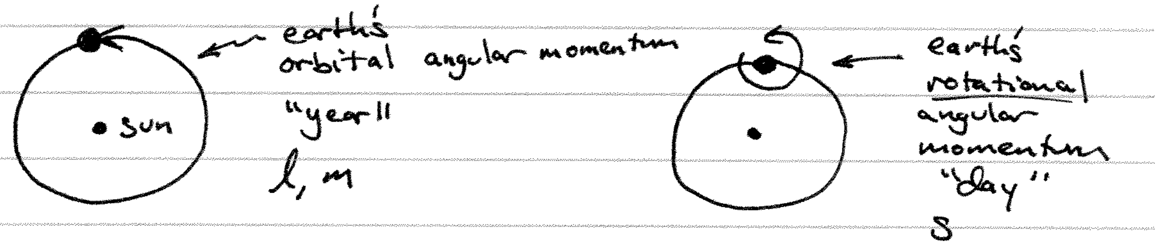
But l is supposed to be an integer?

What Stern & Gerlach discovered is the "spin" of the electrons.

(Actually it had to wait until Goudsmit & Uhlenbeck 3 years later) to identify spin as angular momentum.

Actually, Stern & Gerlach discovered a fundamental property of matter. Spin is an inherent property of particles just like charge and mass. What we see from the Stern-Gerlach experiment is that spin behaves just like an angular momentum.

An analogy (breaks down a bit if you ask too many questions)



Some particles have integer spin, these are Bosons
Some particles have half-integer spin, these are Fermions

Electrons are Fermions with $S = \frac{1}{2}$

Big S = property of particle "total" spin angular momentum

Quantum Numbers $\quad s = -S, -S+1 \ldots S-1, S$

small s

for particles with $S = \frac{1}{2}$

$s = -\frac{1}{2}, +\frac{1}{2}$ ← spin "states"

So our description of the wave function is not quite complete.

$$\Psi(x,y,z,\sigma) = \underbrace{\psi(\overbrace{x,y,z}^{\text{spatial coordinates}})}_{\text{spatial wavefunction}}\alpha(\sigma)$$

spin "up" or $+\frac{1}{2}$ wavefunction (α)

spin coordinate (σ)

<u>or</u>

spin "down" or $-\frac{1}{2}$ wavefunction (β)

$$\Psi(x,y,z,\sigma) = \psi(x,y,z)\beta(\sigma)$$

$$\Psi_{nlms} = \begin{cases} R_{nl}(r)\,Y_l^m(\theta,\phi)\,\alpha(\sigma) & \text{if } s = +\frac{1}{2} \\ R_{nl}(r)\,Y_l^m(\theta,\phi)\,\beta(\sigma) & \text{if } s = -\frac{1}{2} \end{cases}$$

The spin functions are orthonormal:

$$\int \alpha^*(\sigma)\alpha(\sigma)\,d\sigma = 1$$
$$\int \beta^*(\sigma)\beta(\sigma)\,d\sigma = 1$$
$$\int \alpha^*(\sigma)\beta(\sigma)\,d\sigma = \int \beta^*(\sigma)\alpha(\sigma)\,d\sigma = 0$$

So the total wavefunction also remains orthonormal:

$$\int \Psi^*_{100\frac{1}{2}}(\vec{r},\sigma)\,\Psi_{100\frac{1}{2}}(\vec{r},\sigma)\,d\vec{r}\,d\sigma$$

$$= \int_0^\infty r^2 R_{10}^*(r)\,R_{10}(r)\,dr \int_0^\pi \sin\theta \int_0^{2\pi} Y_l^m(\theta,\phi)^* Y_l^m(\theta,\phi)\,d\theta\,d\phi$$

$$* \int \alpha(\sigma)^*\alpha(\sigma)\,d\sigma$$

$$= 1$$

Why does spin matter?

Pauli Exclusion principle:
No fermions can have the same set of quantum numbers. (in the same atom).

This is actually a simplification of a more general rule:
The wave function of a system of fermions must be <u>antisymmetric</u> with respect to interchange of any two identical fermions

That is, for two electron systems:

$$\psi(x_1, x_2) = -\psi(x_2, x_1)$$

This property comes from relativistic quantum field theory, and we're not going to tackle <u>that</u> in this class.

Think on this:

$$\psi(\vec{r}_1, \sigma_1, \vec{r}_2 \sigma_2) = 1s(\vec{r}_1)\alpha(\sigma_1)\, 1s(\vec{r}_2)\beta(\sigma_2)$$

electron 1 in 1s <u>and</u> ↑ electron 2 in 1s <u>and</u> ↓

If we <u>swap</u>, we <u>don't</u> get an antisymmetric wave function. What's <u>wrong</u> with this?

$$\psi(\vec{r}_2 \sigma_2, \vec{r}_1 \sigma_1) = 1s(\vec{r}_2)\alpha(\sigma_2)\, 1s(\vec{r}_1)\beta(\sigma_1)$$