

# *The Hydrogen Atom*

- This is of course the most important model system for understanding electronic structure.
- New wrinkle: we're dealing with a 3D system, instead of the 1D model systems from previous lecture.

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{e^2}{r}$$

- The strategy is to exploit the spherical symmetry of the problem, which allows us to decouple the radial and angular parts of the problem. The angular parts lead to angular momentum eigenstates.

# *The Hamiltonian*

Recall from our previous lecture that the 1D Hamiltonian operator is

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x)$$

By analogy, we can imagine the form of the Hamiltonian for an electron moving around a proton (i.e., H atom):

$$-\frac{\hbar^2}{2m_e} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{e^2}{r}$$

**Kinetic energy term, now in 3D**    **Potential energy**

where  $r$  is the distance between the proton and electron. Actually, this expression would be correct if the proton were infinitely heavy relative to the electron, but that's not quite the case; the correct expression is ...

$$-\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) - \frac{e^2}{r} = -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{r}$$

where  $\mu$  is the “reduced mass” of the system

$$\frac{1}{\mu} = \frac{1}{m_p} + \frac{1}{m_e}$$

which is close to, but not exactly equal to, the electron mass. The origin of our coordinate system is now at the center of mass between the electron and proton, which of course will stay quite close to the proton.

The key to solving the hydrogen atom is to take advantage of the spherical symmetry, i.e., convert to radial coordinates  $(r, \theta, \phi)$ . The potential part of the Hamiltonian is already in radial form, so it's just a matter of getting the kinetic energy operator into the radial coordinates. This is a standard exercise in beginning QM classes, but it is really quite tedious.

The final result is

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

Plugging this into the Hamiltonian yields:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) - \frac{e^2}{r}}_{\text{Purely radial term}} - \frac{\hbar^2}{2\mu r^2} \underbrace{\left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \left( \frac{\partial^2}{\partial \phi^2} \right) \right)}_{\text{Purely angular term}}$$

Purely radial term

Purely angular term

The angular part is often referred to as the “total angular momentum” operator, and gets a special symbol:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) - \frac{e^2}{r}}_{\text{Purely radial term}} + \frac{\hat{L}^2}{2\mu r^2}$$

This separation of variables implies that we can solve independently for the radial and angular eigenfunctions. Neither one of these are trivial derivations, but they are both analytical.

### Angular Part

The potential does not depend on the angles; i.e., there is “free rotation”. These eigenfunctions are the so-called spherical harmonics (maybe think of them as the normal modes of a spherical drum, like a balloon). They are described by 2 quantum numbers:

$$l=0,1,2,3,\dots, \text{ for the } \theta \text{ angle}$$
$$m=0,\pm 1,\pm 2,\dots,\pm l \text{ for the } \phi \text{ angle}$$

and the eigenfunctions take the form

$$Y_l^m(\theta, \phi) = f_l(\theta) e^{im\phi}$$

Now we're dealing with complex-valued eigenfunctions ...

with eigenenergies

$$E = \hbar^2 l(l+1)$$

# Spherical Harmonics

$l=0, m=0$  ("s")

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

$l=1, m=-1,0,+1$  ("p")

$$Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos \theta$$

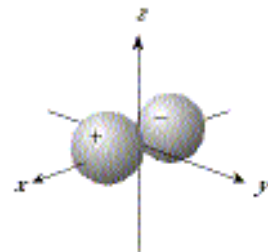
$$p_z = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_1^{+1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{i\varphi} \quad \Rightarrow$$

$$p_x = \sqrt{\frac{3}{8\pi}} \sin \theta \cos \varphi$$

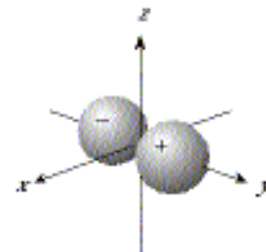
$$Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\varphi}$$

$$p_y = \sqrt{\frac{3}{8\pi}} \sin \theta \sin \varphi$$



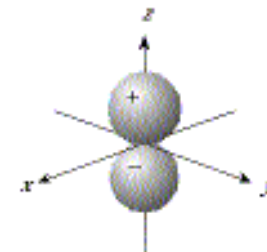
$p_x$

(a)



$p_y$

(b)



$p_z$

(c)

# *d orbitals*

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

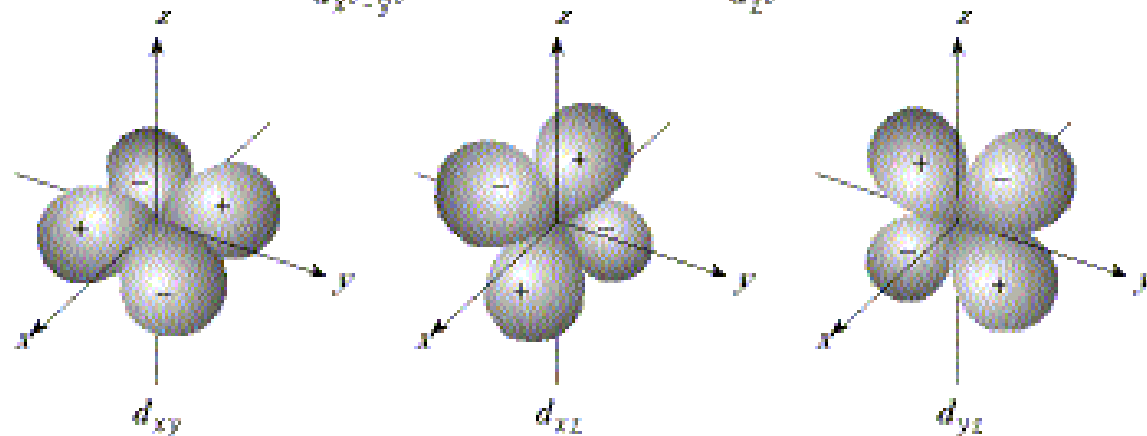
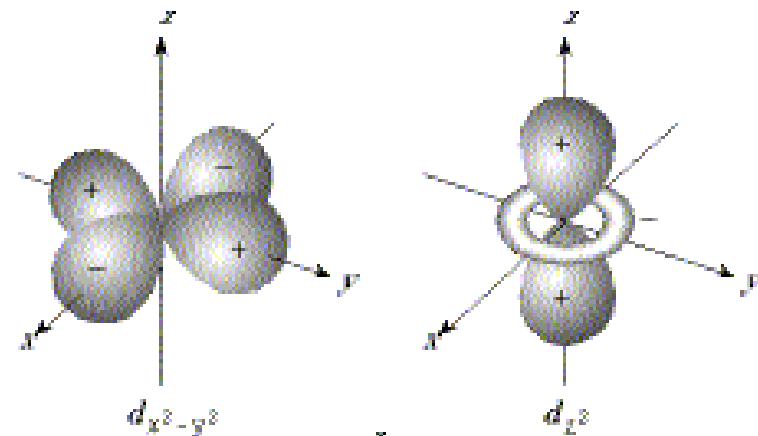
$$Y_2^0 = \sqrt{\frac{5}{16\pi}} (3\cos^2 \theta - 1)$$

$$Y_2^{+1} = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{i\varphi}$$

$$Y_2^{-1} = \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{-i\varphi}$$

$$Y_2^{+2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{2i\varphi}$$

$$Y_2^{-2} = \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{-2i\varphi}$$



## *Knowing the Angular Eigenfunctions, We Can Now Do Radial Part*

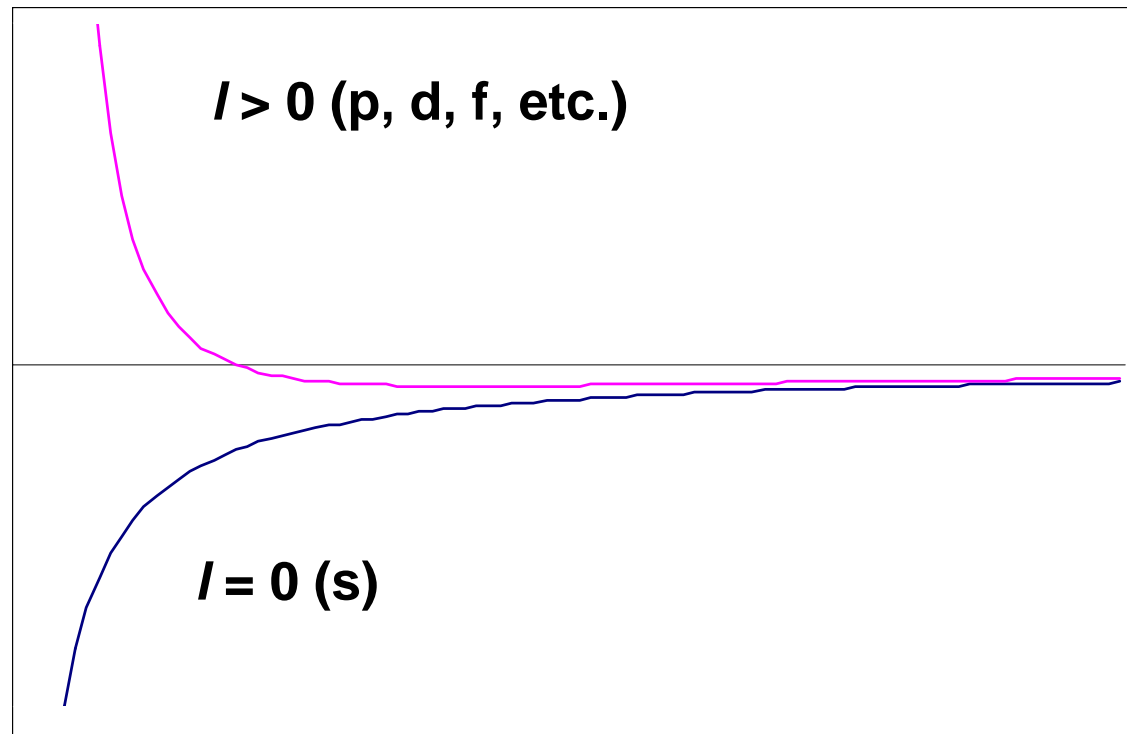
$$\hat{H} = \boxed{-\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) - \frac{e^2}{r}} + \frac{\hat{L}^2}{2\mu r^2} \quad \psi(r, \theta, \varphi) = \psi_r(r) Y_l^m(\theta, \varphi)$$

$$\begin{aligned} \hat{L}^2 \psi(r, \theta, \varphi) &= \psi_r(r) \hat{L}^2 Y_l^m(\theta, \varphi) \\ &= \psi_r(r) \hbar^2 l(l+1) Y_l^m(\theta, \varphi) \\ &= \hbar^2 l(l+1) \psi(r, \theta, \varphi) \end{aligned}$$

$$\hat{H} \psi(r, \theta, \varphi) = \left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) - \frac{e^2}{r} + \frac{\hbar^2 l(l+1)}{2\mu r^2} \right] \psi_r(r) \quad \text{purely radial!}$$

“Effective potential”, incorporating a “centrifugal force”. Solve for each value of  $l$ .

# Centrifugal Force in H-atom



- For  $l=0$ , wavefunction is always a maximum at  $r = 0$ .
- For  $l>0$ , wavefunction is always zero at  $r = 0$ .

# *Radial eigenfunctions of H atom*

The eigenenergies are simple, and do not depend on  $l$  ...

$$E = -\frac{C}{n^2}$$

where  $C$  is a constant that involves the reduced mass, electron charge, and Planck's constant.

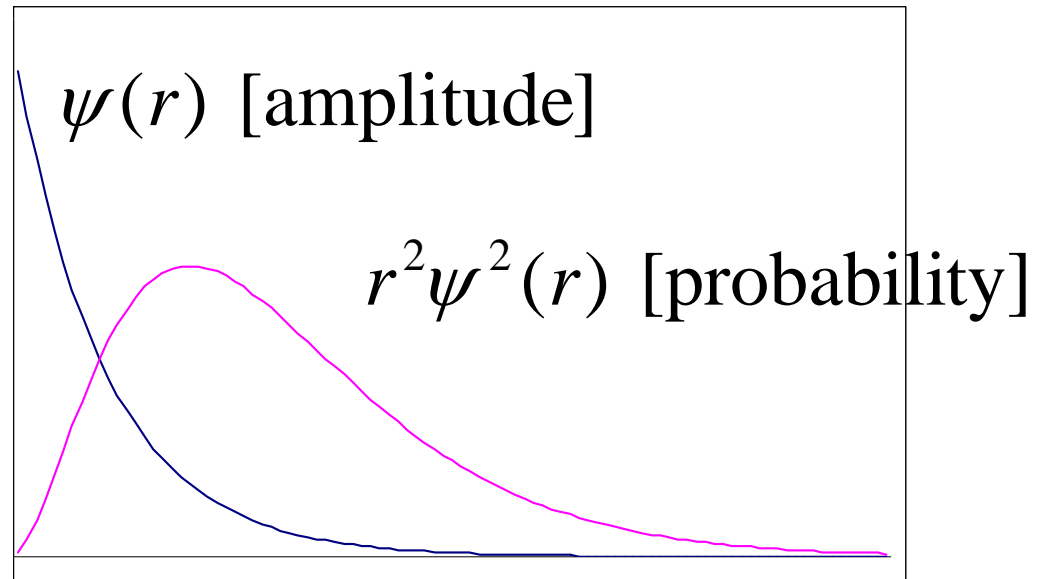
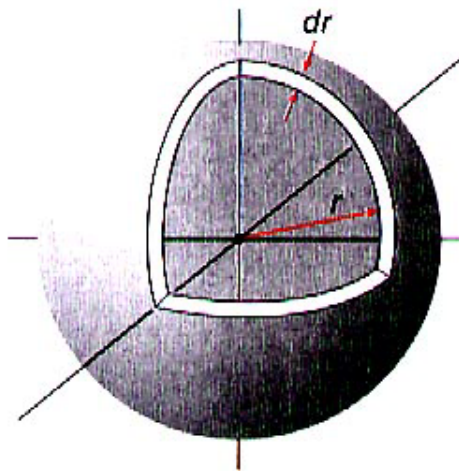
The eigenfunctions are pretty awful, and do depend on  $l$  ...

$$R_{nl}(r) = -C_{nl} r^l e^{-r/na_0} L_{n+l}^{2l+1} \left( \frac{2r}{na_0} \right)$$

where  $C_{nl}$  is a complicated “normalization constant”, and  $L$  are the “associated Laguerre functions”, and  $a_0$  is the “Bohr radius”, a constant.

# Ground state of H atom

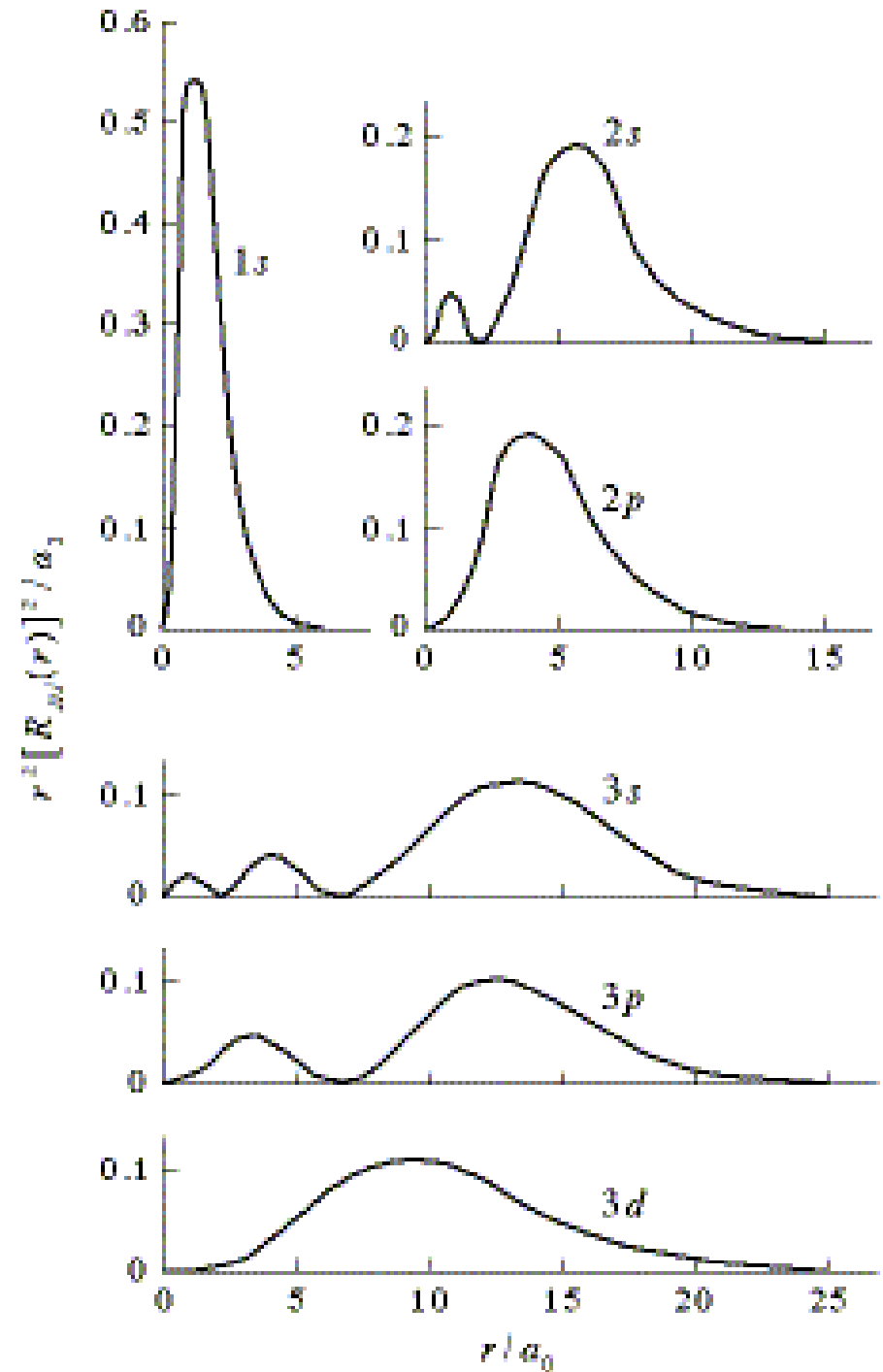
$$R_{00}(r) = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{\frac{3}{2}} e^{-r/a_0}$$



*Amplitude at  $r=0$  is large, but probability of finding system there is zero!*

## Some more H atom wavefunctions

1. For constant  $l$ , number of nodes along  $r$  increases with increasing  $n$ .
2. For  $l=n$ , all nodes are in the angular coordinates (2p, 3d, etc.).



# *Only a very few, very simple QM systems can be solved analytically*

The ones we've just looked at are analytical, or at least quasi-analytical, as is the hydrogen atom, which we will review in the next lecture. But that's about it for analytical solutions. Everything else involves some numerical computation. The indispensable tools for modern quantum mechanics are perturbation theory and the variational principle.

## Perturbation theory

- Relates the solutions of one QM problem to another that has already been solved (“reference system”).
- Works well when the 2 QM systems are similar to each other, i.e., the one you are trying to solve represents a relatively small “perturbation” relative to the reference system.
- For example, the eigenstates of the anharmonic (Morse) oscillator can be solved using the harmonic oscillator as the reference system. Works well for the first few eigenstates, but not near dissociation.

# Basics of Perturbation Theory

$$\hat{H} = \hat{H}^\circ + \hat{H}'$$

Divide the Hamiltonian into two parts: A “zero-order” Hamiltonian whose eigenstates you know, and a “perturbation”.

$$\hat{H}^\circ \psi^\circ = E^\circ \psi^\circ$$

$$\psi = \psi^\circ + \psi' \quad E = E^\circ + E'$$

Write the eigensolutions of the full system as sum of the zero-order solutions and a perturbation.

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

these terms equal

$$\hat{H}^\circ \psi^\circ + \hat{H}' \psi^\circ + \hat{H}^\circ \psi' + \hat{H}' \psi' = E^\circ \psi^\circ + E' \psi^\circ + E^\circ \psi' + E' \psi'$$

2nd order terms

Substitute into Schrodinger eqn. and simplify.

$$\hat{H}' \psi^\circ + \hat{H}^\circ \psi' \approx E' \psi^\circ + E^\circ \psi'$$

$$\int \psi^\circ \hat{H}' \psi^\circ + \int \psi^\circ \hat{H}^\circ \psi' \approx \int \psi^\circ E' \psi^\circ + \int \psi^\circ E^\circ \psi'$$

this term is exactly zero

$$\int \psi^\circ \hat{H}' \psi^\circ + \int \psi^\circ (\hat{H}^\circ - E^\circ) \psi' \approx E' \int \psi^\circ \psi^\circ$$

integrated probability is 1

$$\int \psi^\circ \hat{H}' \psi^\circ \approx E'$$

# More Advanced Perturbation Theory

$$\Delta E_n = \int \psi_n^0 \hat{H}' \psi_n^0 + \sum_{j \neq n} \frac{\left| \int \psi_j^0 \hat{H}' \psi_n^0 \right|^2}{E_n^0 - E_j^0}$$

2nd order term

$$\psi_n = \psi_n^0 + \sum_{j \neq n} \frac{\int \psi_j^0 \hat{H}' \psi_n^0}{E_n^0 - E_j^0} + \dots$$

perturbation theory  
can be applied to  
eigenfunctions as well  
as eigenenergies

## Variational principle

- A very important theorem in modern quantum mechanics.
- Provides an upper bound to the eigenenergies.
- The basic strategy is to “guess” a wavefunction and obtain its energy using your Hamiltonian operator. This energy will always be larger than the true eigenenergy. Moreover, the energy will approach the true energy as the trial wavefunction becomes more like the true wavefunction.

$$E_0 = \frac{\int \psi_0 \hat{H} \psi_0}{\int \psi_0 \psi_0} \quad E_\phi = \frac{\int \phi \hat{H} \phi}{\int \phi \phi} \quad E_\phi \geq E_0$$

- The usual approach is to define the trial wavefunction as a linear superposition of multiple “basis functions” with linear “variational parameters”, i.e.,

$$\varphi = \sum_{n=1}^N c_n f_n$$

- It is fairly easy to show that the energy will reach a minimum when the determinant of this matrix is zero:

# Simple Example: Trial Wavefunction with 2 Basis Functions

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

$$\begin{aligned} E_\phi &= \frac{\int \phi \hat{H} \phi}{\int \phi \phi} \\ &= \frac{\int (c_1 f_1 + c_2 f_2) \hat{H} (c_1 f_1 + c_2 f_2)}{\int (c_1 f_1 + c_2 f_2)(c_1 f_1 + c_2 f_2)} \\ &= \frac{c_1^2 \int f_1 \hat{H} f_1 + c_1 c_2 \int f_1 \hat{H} f_2 + c_1 c_2 \int f_2 \hat{H} f_1 + c_2^2 \int f_2 \hat{H} f_2}{c_1^2 \int f_1 f_1 + c_1 c_2 \int f_1 f_2 + c_1 c_2 \int f_2 f_1 + c_2^2 \int f_2 f_2} \\ &= \frac{c_1^2 H_{11} + c_1 c_2 H_{12} + c_1 c_2 H_{21} + c_2^2 H_{22}}{c_1^2 S_{11} + c_1 c_2 S_{12} + c_1 c_2 S_{21} + c_2^2 S_{22}} \end{aligned}$$

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

Taking advantage of the variational principle, we aim to minimize this expression with respect to the “variational parameters”  $c_1$  and  $c_2$ , i.e.,

$$\frac{\partial E_{\phi}}{\partial c_1} = 0$$

$$\frac{\partial E_{\phi}}{\partial c_2} = 0$$

These two expressions lead to the following linear equations:

$$c_1(H_{11} - ES_{11}) + c_2(H_{21} - ES_{21}) = 0$$

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

This now becomes a standard problem in linear algebra, which can be expressed as a matrix problem.

# Matrix Formulation of Quantum Eigenvalue Problem

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots \\ \vdots & \vdots & \ddots \end{vmatrix} = 0$$

$$H_{ij} = \int f_i \hat{H} f_j$$

$$S_{ij} = \int f_i f_j$$

If basis set is chosen to be “orthonormal”, i.e.,

$$S_{ij} = \delta_{ij}$$

$$\begin{vmatrix} H_{11} - E & H_{12} & \cdots \\ H_{21} & H_{22} - E & \cdots \\ \vdots & \vdots & \ddots \end{vmatrix} = 0$$

Except for very simple problems, solving these equations (essentially root finding of polynomial equation) is handled numerically (e.g., Householder diagonalization).