A quick example of a Non-Linear Variation is using the exact form of the ground state wavefunction for a hydrogen-like atom or ion.

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{r} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{2r^2}\frac{L^2(\theta,\varphi)}{}$$

If we didn't know that $\varphi_0 = e^{-\frac{Zr}{a}} = e^{-Zr}$ in atomic units, then we might guess that:

$$\phi_{trial} = e^{-\frac{\alpha r}{a}} = e^{-\alpha r} \text{ in atomic units}$$

$$\frac{\int \varphi_{trial}^* H \varphi_{trial}\, d\tau}{\int \varphi_{trial}^* \varphi_{trial} d\tau} = \langle E \rangle$$

$$d\tau = r^2 dr \sin\theta\, d\phi$$

$$\langle E \rangle = \frac{\int e^{-\alpha r} H e^{-\alpha r}\, d\tau}{\int e^{-\alpha r} e^{-\alpha r} d\tau} = \frac{\int e^{-\alpha r}\left(-\frac{\partial^2}{2\partial r^2} - \frac{\partial}{r\partial r} - \frac{Z}{r}\right) e^{-\alpha r}\, 4\pi^2 r^2 dr}{\int e^{-2\alpha r} 4\pi^2 r^2 dr}$$

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$$\langle E \rangle = \frac{\int e^{-\alpha r} H e^{-\alpha r} \, d\tau}{\int e^{-\alpha r} e^{-\alpha r} d\tau} = \frac{\int e^{-\alpha r}\left(-\dfrac{\partial^2}{2\partial r^2} - \dfrac{\partial}{r\partial r} - \dfrac{Z}{r}\right)e^{-\alpha r}\, 4\pi^2 r^2 dr}{\int e^{-2\alpha r}\, 4\pi^2 r^2 dr}$$

$$= \frac{-\frac{\alpha^2}{2}\int e^{-2\alpha r} r^2 dr + \alpha \int e^{-2\alpha r} r \, dr - Z\int e^{-2\alpha r} r \, dr}{\int e^{-2\alpha r} r^2 dr}$$

$$\int_0^\infty r^n e^{-br} dr = \frac{n!}{b^{n+1}}$$

$$\text{For n} = 1: \quad \frac{1!}{b^{1+1}} = \frac{1}{b^2} = b^{-2} \qquad \text{units } = \text{length}^2$$

$$\text{For n} = 2: \quad \frac{2!}{b^{2+1}} = \frac{2}{b^3} = 2b^{-3} \quad \text{units } = \text{length}^3$$

$$\int_0^\infty r^n e^{-br} dr = \frac{n!}{b^{n+1}}$$

For $n = 1$: $\dfrac{1!}{b^{1+1}} = \dfrac{1}{b^2} = b^{-2}$ units $= \text{length}^2$

For $n = 2$: $\dfrac{2!}{b^{2+1}} = \dfrac{2}{b^3} = 2b^{-3}$ units $= \text{length}^3$

$$\int_0^\infty e^{-2\alpha r} r^2 dr = \frac{2}{(2\alpha)^3} = 2(2\alpha)^{-3}$$

$$\int_0^\infty e^{-2\alpha r} r \, dr = (2\alpha)^{-2}$$

$$\frac{-\alpha^2/2 \int_0^\infty e^{-2\alpha r} r^2 dr + \alpha \int_0^\infty e^{-2\alpha r} r \, dr - Z \int_0^\infty e^{-2\alpha r} r \, dr}{\int_0^\infty e^{-2\alpha r} r^2 dr}$$

$$\frac{\left(-\alpha^2/2\right) 2(2\alpha)^{-3} + \alpha(2\alpha)^{-2} - Z(2\alpha)^{-2}}{2(2\alpha)^{-3}} = -\alpha^2/2 + (\alpha/2)2\alpha - Z\alpha$$

$$\langle E \rangle = \alpha^2/2 - Z\alpha$$

$$\langle E \rangle = \frac{\alpha^2}{2} - Z\alpha = T_{approx} + V_{approx}$$

$$\frac{\partial \langle E \rangle}{\partial \alpha} = \frac{2\alpha}{2} - Z = \alpha - Z = 0$$

Therefore, the value of α giving the lowest (or highest) = Z, which we know is also the exactly correct solution.

Note: Because 1s(r) = proportional to $e^{-\alpha r}$, α has units of length^{-1} and α^2 has units of length^{-2}, i.e., the same units as $-\frac{\hbar^2 \partial^2}{2m \partial r^2}$ **in atomic units.**

The He Atom

Another interesting example is the He atom. Consider the simple product function,

$$\psi = N\, e^{-\alpha r_1}\, e^{-\alpha r_2}$$

The energy obtained with various wavefunctions are as follows:

ψ	E
α = 2 (the right value for He+)	−2.75
α = 1.6875*	−2.848
Hartree SCF (table of numbers)	−2.86
Exact (Experiment)	−2.90

This assumes the presence of another electron does not affect the size of the orbital

Lowest E by varying α

This means use $\Psi = f(r_1)\, f(r_2)$ with **NO restrictions** on the shape f(r)

The Hartree SCF wavefunction, whose <u>only</u> restriction is that

ψ = product of orbitals $\phi_{1s}(1)\ \phi_{1s}(2)$ and allows any shape whatsoever for ϕ_{1s}, cannot give the right answer! This proves, to me anyway, that we must think of the electrons in atoms as point charges which do dodge one another because of the repulsion. The motion is <u>correlated</u>; they, to some extent, stay on opposite sides of the atom. By doing so, the energy is lowered by .04 a.u. = ~1ev = 23 kcal/mole.

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That is called the correlation energy and is never accounted for by a single configuration, product-of-orbitals type wavefunction. In the Chemistry literature you will more and more run into the term configuration-interaction (CI). The reason is that, by making a linear combination of configurations, electron correlation is introduced. That is by using

$$\psi = c_1 \phi_{1s}(1) \phi_{1s}(2) + c_2 \phi_{2s}(1) \phi_{2s}(2) + c_3 \phi_{2p}(1) \phi_{2p}(2) + \cdots$$

and varying the coefficients, c_1, c_2, c_3 . . . . , one may obtain the exact energy if enough configurations are used. This is also known as mixing configurations.

Linear Variation Method

The vast majority of variation calculations done by chemists involve the linear variation method, an example of which was just given. It is also the basis for constructing molecular orbitals (MO's) from atomic orbitals (AO's). The general idea is to construct ψ as

$$\psi = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + \cdots\cdots$$

and find the "best" ψ by varying the c_i's until the energy is a minimum. The ϕ_i's are called the basis set or the basis functions. They are usually AO's if constructing MO's, or configurations if constructing a many-electron wavefunction. They obviously must all be the same thing (you can't add apples and oranges).

You are going to be asked to develop an "intuition" about doing linear variation calculations involving just two basis functions, a little like learning the multiplication table (and certainly not more difficult).

Only by doing this will you start to feel comfortable with quantum chemistry.

Your goal is to become so familiar with the pattern of results that they become *simple truths* to you. **You will be able to predict the nature of mixing of wave functions, and splitting of energy levels.**

The General Form –

Well, almost general. We will work only with real functions to make the notation *easier* . We said

$$\psi = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + \ldots\ldots$$

We need to write

$$E = \frac{\int \psi \mathcal{H} \psi \, dv}{\int \psi \psi \, dv}$$

as a function of the c_i's and then <u>minimize</u>   E with respect to varying each c_i. Unique values of the c_i's are not found, but a unique <u>ratio</u> of c_i's is found. All this means is that the resulting ψ will not necessarily be normalized; we can *normalize* easily if you know the ratio of c_i's. Thus, substituting for ψ

$$E = \frac{\int (c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + \ldots) \mathcal{H} (c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_1 + \ldots)}{\int (c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + \ldots)^2 \, dv}$$

Now define $H_{ij} =$ $\int \phi_i \mathcal{H} \phi_j \, dv$

and $S_{ij} =$ $\int \phi_i \phi_j \, dv$

H_{ij} is called the Hamiltonian matrix element between ϕ_i and ϕ_j; it is also referred to as the interaction between ϕ_i and ϕ_j. S_{ij}, you should recognize as the overlap integral of ϕ_i and ϕ_j. With these definitions we get:

$$E = c_1 c_1 H_{11} + c_2 c_2 H_{22} + c_3 c_3 H_{33} + \ldots \ldots$$
$$+ c_1 c_2 H_{12} + c_1 c_3 H_{13} + c_2 c_3 H_{23} + \ldots \ldots$$
$$+ c_2 c_1 H_{21} + c_3 c_1 H_{31} + c_3 c_2 H_{32} + \ldots \quad \text{all divided by:}$$

$$c_1 c_1 S_{11} + c_2 c_2 S_{22} + c_3 c_3 S_{33} + \ldots \ldots$$
$$+ c_1 c_2 S_{12} + c_1 c_3 S_{13} + c_2 c_3 S_{23} + \ldots \ldots$$
$$+ c_2 c_1 S_{21} + c_3 c_1 S_{31} + c_3 c_2 S_{32} + \ldots \ldots$$

But, since we are using real functions $S_{12} = S_{21}$ and $H_{12} = H_{21}$ so we can rewrite E as

$$E = \frac{c_1^2 H_{11} + c_2^2 H_{22} + \ldots \ldots + 2c_1 c_2 H_{12} + 2c_1 c_3 H_{13} + \ldots \ldots}{c_1^2 S_{11} + c_2^2 S_{22} + \ldots \ldots \quad 2c_1 c_2 S_{12} + 2c_1 c_3 S_{13} + \ldots \ldots}$$

$$= \frac{\text{Top}}{\text{Bottom}}$$

Now we wish to find the slope of E with respect to each c_i and set it

$= 0$,* i.e., $\dfrac{\partial E}{\partial c_i} = 0$ for each c_i

But recall the formula for the derivative of a quotient:

$$\frac{\partial E}{\partial c_i} = \frac{1}{\text{Bottom}} \, \frac{\partial \, \text{Top}}{\partial c_i} + \text{Top} \, \frac{\partial \, \frac{1}{\text{Bottom}}}{\partial c_i} = 0$$

$$= \frac{1}{\text{Bottom}} \, \frac{\partial \, \text{Top}}{\partial c_i} - \frac{\text{Top}}{(\text{Bottom})^2} \, \frac{\partial \, \text{Bottom}}{\partial c_i} = 0$$

⟵ This is the condition for the Energy to by a minimum.

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and after multiplying by Bottom on both sides and recognizing that

$$E = \frac{Top}{Bottom}$$

we get:

$$\frac{\partial\, Top}{\partial\, c_i} - E\, \frac{\partial\, Bottom}{\partial\, c_i} = 0$$

Now note that $\qquad \dfrac{\partial\, Top}{\partial c_1} = 2H_{11}c_1 + 2H_{12}c_2 + 2H_{13}c_3 + \ldots$

or $\qquad \dfrac{\partial\, Top}{\partial c_i} = 2H_{i1}c_1 + 2H_{i1}c_2 + 2H_{i3}c_3 + \ldots$

and likewise for $\quad \dfrac{\partial\, Bottom}{\partial c_i}$.

Now, after dividing by 2 on both sides, one has n equations of the form:

$$H_{i1}c_1 + H_{i2}c_2 + \ldots\ldots H_{in}c_n - E(S_{i1}c_1 + S_{i2}c_2 + \ldots S_{in}c_n) = 0$$

$$\text{for } i = 1 \text{ to } n$$

This may be compacted slightly as $\qquad \displaystyle\sum_j (H_{ij} - ES_{ij})\, c_j = 0$

$$\text{for } i = 1 \text{ to } n$$

For a case of 3 basis functions it looks like this:

$$(H_{11} - S_{11}E)c_1 + (H_{12} - S_{12}E)c_2 + (H_{13} - S_{13}E)c_3 = 0$$

$$(H_{21} - S_{21}E)c_1 + (H_{22} - S_{22}E)c_2 + (H_{23} - S_{23}E)c_3 = 0$$

$$(H_{31} - S_{31})c_1 + (H_{32} - S_{32}E)c_2 + (H_{33} - S_{33}E)c_3 = 0$$

Almost always we will use an orthonormal basis set, which means:
$S_{ii} = 1$ and $S_{ij} = 0$ if i not equal j

$$(H_{11} - E)c_1 + (H_{12})c_2 + (H_{13})c_3 = 0$$

$$(H_{21})c_1 + (H_{22} - E)c_2 + (H_{23})c_3 = 0$$

$$(H_{21})c_1 + (H_{32})c_2 + (H_{33} - E)c_3 = 0$$

A set of N simultaneous homogeneous linear equations

THIS IS WHAT YOU WANT TO MEMORIZE!

Case of Two Orthonormal Functions

Now if we choose $\psi = c_1 \phi_1 + c_2 \phi_2$ for such a basis we immediately know to write:

$$(H_{11} - E)c_1 + H_{12}c_2 = 0$$

$$H_{21}c_1 + (H_{22} - E)c_2 = 0$$

We shall call $H_{12} = H_{21} = \beta$ and $H_{11} = \alpha_1$, $H_{22} = \alpha_2$ and for these discussions pick $\alpha_1 < \alpha_2$.

$$
\begin{aligned}
(H_{11} - E)c_1 \;+\; (H_{12})c_2 \;&=\; 0 \\
(H_{21})c_1 \;+\; (H_{22} - E)c_2 \;&=\; 0
\end{aligned}
\qquad = \qquad
\begin{aligned}
(\alpha_1 - E)c_1 \;+\; \beta c_2 \;&=\; 0 \\
\beta c_1 \;+\; (\alpha_1 - E)c_2 \;&=\; 0
\end{aligned}
$$

Language: α_1 is called the "energy of φ_1, α_2 is called the "energy of φ_2 and β **is the "interaction of φ_1 and φ_1**

What is always the requirement to solve
 set of N simultaneous homogeneous linear equations?

**THE DETERMINANT of the MATRIX OF NUMBERS
MULTIPLYING THE COEFFICIENTS MUST = 0**

or $(\alpha_1 - E)(\alpha_2 - E) - \beta^2 = 0$

or $E^2 - (\alpha_1 + \alpha_2)E + \alpha_1\alpha_2 - \beta^2 = 0$

or $a E^2 + b E + c = 0$

The quadratic formula then says

$$E = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{(\alpha_1 + \alpha_2)}{2} \pm \frac{1}{2}\sqrt{(\alpha_1 + \alpha_2)^2 - 4\alpha_1\alpha_2 + 4\beta^2}$$
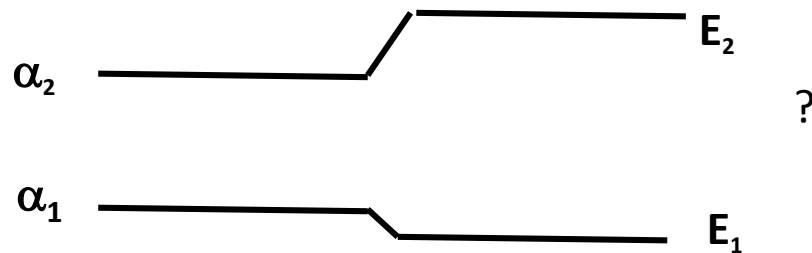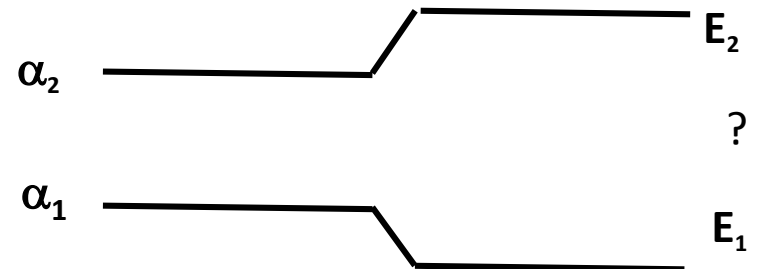
which can be shown to be

$$E = \frac{\alpha_1 + \alpha_2}{2} \pm \sqrt{\left(\frac{\alpha_1 - \alpha_2}{2}\right)^2 + \beta^2}$$

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Making the transformation to this very useful form will be part of the next homework.

What does it tell you when the two energies are degenerate?

the splitting is just 2β and $E = \alpha \pm \beta$.
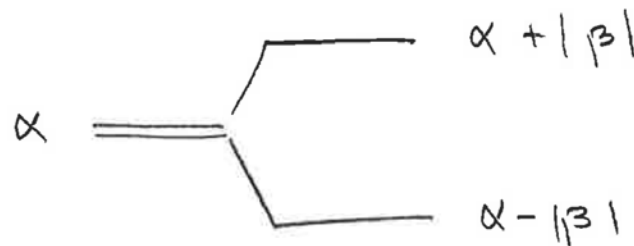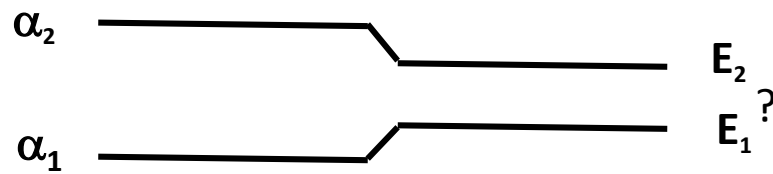
$$E = \frac{\alpha_1 + \alpha_2}{2} \pm \sqrt{\left(\frac{\alpha_1 - \alpha_2}{2}\right)^2 + \beta^2}$$

What if α_1 and α_2 different?

What if α_1 and α_2 different?

α_2 E_2
     ?
α_1 E_1

E_2

α_2

α_1 E_1

?

α_2 E_2

?

α_1 E_1

$$E = \frac{\alpha_1 + \alpha_2}{2} \pm \sqrt{\left(\frac{\alpha_1 - \alpha_2}{2}\right)^2 + \beta^2}$$

What if α_1 and α_2 different?
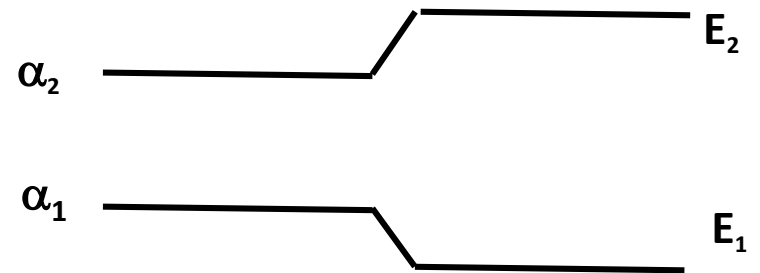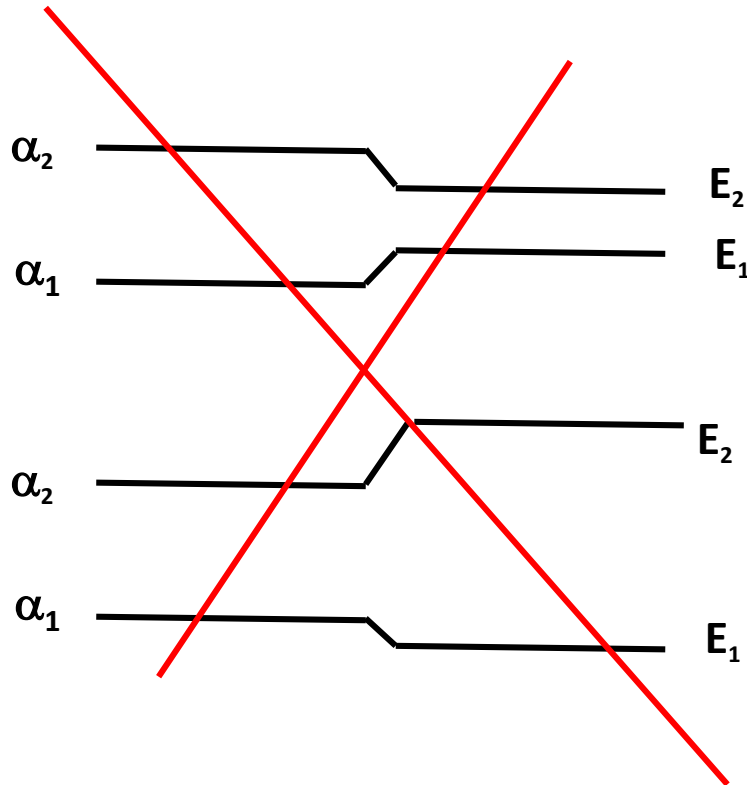
Always!

The next homework will teach you more details, and on a couple quizzes you will be asked to solve 3 of these 2 x 2 in a few minutes—after a training session or two ☺.