In a famous paper published in 1929, Dirac wrote:

"The underlying physical laws necessary for the mathematical theory of ... the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

With the help of computers, we can now solve many of the problems that Dirac considered insoluble in 1929. The most important tools for this purpose are the Variation Method and Perturbation Theory. Here we examine the first of these and show how it leads to the ideas that we use to understand chemical bonding.

The Variation Method is based on the *variation principle*.

This asserts that if $\tilde{\psi}$ is an arbitrary wavefunction satisfying the boundary conditions for the problem, then the expectation value of its energy is not less than the lowest eigenvalue of the Hamiltonian.

(1)

That is,

$$\tilde{E} \equiv \frac{\left\langle \tilde{\psi} \left| H \left| \tilde{\psi} \right\rangle \right\rangle}{\left\langle \tilde{\psi} \left| \tilde{\psi} \right\rangle \right\rangle} \ge E_{0}$$

where E_0 is the lowest eigenvalue of H

Proof

Expand $\tilde{\psi}$ in terms of the normalized eigenfunctions of *H*

 $\tilde{\psi} = \sum_{k} c_{k} \psi_{k}$

If H is any linear Hermitian operator that represents a physically observable property, then the eigenfunctions of H form a complete set.

$$egin{aligned} &\left\langle ilde{oldsymbol{\psi}} \left| ilde{oldsymbol{\psi}}
ight
angle &= \sum_{kl} c_k^{\ *} c_l \left\langle ilde{oldsymbol{\psi}}_k \left| ilde{oldsymbol{\psi}}_l
ight
angle \ &= \sum_{kl} c_k^{\ *} c_l \delta_{kl} \ &= \sum_k \left| c_k \right|^2 \end{aligned}$$

$$\begin{split} \left\langle \tilde{\psi} \left| H \left| \tilde{\psi} \right\rangle &= \sum_{kl} c_k^{*} c_l \left\langle \psi_k \left| H \left| \psi_l \right\rangle \right. \right. \right. \\ &= \sum_{kl} c_k^{*} c_l \left\langle \psi_k \left| E_l \left| \psi_l \right\rangle \right. \\ &= \sum_{kl} c_k^{*} c_l E_l \delta_{kl} \\ &= \sum_k \left| c_k \right|^2 E_k \end{split}$$

so that

$$\tilde{E} = \frac{\left\langle \tilde{\psi} \left| H \left| \tilde{\psi} \right\rangle \right\rangle}{\left\langle \tilde{\psi} \left| \tilde{\psi} \right\rangle \right\rangle} = \frac{\sum_{k} \left| c_{k} \right|^{2} E_{k}}{\sum_{k} \left| c_{k} \right|^{2}}$$

$$\tilde{E} - E_{0} = \frac{\sum_{k} \left| c_{k} \right|^{2} E_{k}}{\sum_{k} \left| c_{k} \right|^{2}} - \frac{\sum_{k} \left| c_{k} \right|^{2} E_{0}}{\sum_{k} \left| c_{k} \right|^{2}} = \frac{\sum_{k} \left| c_{k} \right|^{2} \left(E_{k} - E_{0} \right)}{\sum_{k} \left| c_{k} \right|^{2}} \ge 0$$

if E_0 is the ground-state energy. Note that $\tilde{E} = E_0$ only if all the c_k are zero for states with $E_k > E_0$. To get the energy exactly right we have to get the wavefunction exactly right. However a good approximation to the wavefunction will yield a good approximation to the energy.

To arrive at good approximation to the ground state energy E, we try many trial variation functions and look for the one that gives the lowest value of the variational integral.

Variation principle for a particle in a box

Suppose that we did not know the ground-state wavefunction for a particle in a box. Knowing that it has to be zero when x = 0 and x = a, we might try the wavefunction $\tilde{\psi} = x(a - x)$. For this wavefunction we find

$$\langle \tilde{\psi} | \tilde{\psi} \rangle = \int_{0}^{a} x^{2} (a - x)^{2} dx = a^{5} / 30$$

$$\langle \tilde{\psi} | H | \tilde{\psi} \rangle = -\frac{\hbar^{2}}{2m} \int_{0}^{a} x (a - x) \frac{d^{2}}{dx^{2}} x (a - x) dx = \frac{\hbar^{2}}{2m} \frac{a^{3}}{3}$$

$$\tilde{E} = \langle H \rangle = \frac{\langle \tilde{\psi} | H | \tilde{\psi} \rangle}{\langle \tilde{\psi} | \tilde{\psi} \rangle} = 10\hbar^{2} / 2ma^{2}$$

$$0 \qquad l$$

The exact energy for the ground state in this case is $h^2/8ma^2$, so the approximate result is higher than the exact one by a factor of $10/\pi^2 = 1.013$. The wavefunction is not correct, but it gives a good estimate of the energy.

Usually we use a trial function that contains one or more adjustable parameters, and minimize the energy with respect to the parameters. We can use the variation method in this way to find the harmonic oscillator ground state, using the trial function $\tilde{\psi} = e^{-\frac{1}{2}\alpha x^2}$.

$$H\tilde{\psi} = \frac{\hbar^2 \alpha}{2m} \tilde{\psi} + \frac{1}{2} x^2 \left[k - \frac{\alpha^2 \hbar^2}{m} \right] \tilde{\psi}$$
$$\int \tilde{\psi}^* H\tilde{\psi} dx = \frac{\hbar^2 \alpha}{2m} \sqrt{\pi / \alpha} + \frac{1}{2} \left[k - \frac{\alpha^2 \hbar^2}{m} \right] \frac{\sqrt{\pi / \alpha}}{2\alpha}$$

Also $\int \tilde{\psi}^* \tilde{\psi} \, \mathrm{d}x = \sqrt{\pi/\alpha}$

$$\tilde{E} = \frac{\left\langle \tilde{\psi} \left| H \left| \tilde{\psi} \right\rangle \right\rangle}{\left\langle \tilde{\psi} \left| \tilde{\psi} \right\rangle \right\rangle} = \frac{\hbar^2 \alpha}{2m} + \frac{1}{4\alpha} \left[k - \frac{\alpha^2 \hbar^2}{m} \right] = \frac{\hbar^2 \alpha}{4m} + \frac{k}{4\alpha}$$

$$\tilde{E} = \frac{\left\langle \tilde{\psi} \left| H \left| \tilde{\psi} \right\rangle \right\rangle}{\left\langle \tilde{\psi} \left| \tilde{\psi} \right\rangle \right\rangle} = \frac{\hbar^2 \alpha}{2m} + \frac{1}{4\alpha} \left[k - \frac{\alpha^2 \hbar^2}{m} \right] = \frac{\hbar^2 \alpha}{4m} + \frac{k}{4\alpha}$$

To find the lowest energy, we minimize with respect to α and easily find that $\alpha = \sqrt{km}/\hbar$, as before.

The first term in \tilde{E} is the expectation value $\langle T \rangle$ of the kinetic energy, while the second term is the expectation value $\langle V \rangle$ of the potential energy. If α is large, we get a sharply peaked $\tilde{\psi}$ which has a low potential energy but a high kinetic energy. If α is small, the wave function is broad and varies slowly with x, so $\langle T \rangle$ is small, but it extends into regions where the potential energy is high.



Linear combination of atomic orbitals

Usually we choose a trial wavefunction that has one or more adjustable parameters in it, and choose values for the parameters that minimize the energy. An very important type of trial function is the *linear combination of atomic orbitals* (L.C.A.O.), which we can illustrate for the hydrogen molecule ion.

The wavefunction for an individual hydrogen atom is the 1*s* orbital; for a hydrogen molecule ion we try the wavefunction

 $\tilde{\psi} = c_a s_a + c_b s_b$

where s_a is the normalized 1s orbital for atom a and s_b for atom b, and c_a and c_b are numerical coefficients that we shall adjust to minimize the energy. This function behaves like s_a near nucleus a, where s_b is small, and like s_b near nucleus b. The energy \tilde{E} for the L.C.A.O. trial function is

$$\tilde{E} = \frac{\left\langle \tilde{\psi} \left| H \left| \tilde{\psi} \right\rangle \right\rangle}{\left\langle \tilde{\psi} \left| \tilde{\psi} \right\rangle \right\rangle} = \frac{\int (c_a s_a + c_b s_b) H (c_a s_a + c_b s_b) d\tau}{\int (c_a s_a + c_b s_b) (c_a s_a + c_b s_b) d\tau} = \frac{\left(c_a^2 + c_b^2\right) \alpha + 2c_a c_b \beta}{c_a^2 + c_b^2 + 2c_a c_b S}$$
$$\alpha = \int s_a H s_a d\tau = \int s_b H s_b d\tau$$
$$\beta = \int s_a H s_b d\tau = \int s_b H s_a d\tau$$
$$S = \int s_a s_b d\tau$$

 α is the energy of the hydrogen 1s orbital, somewhat modified because the Hamiltonian is for the molecule, not the atom. β is the energy of the overlap density in the field of the molecule; it describes the strength of the bonding, and like α it is negative. S is the *overlap integral*, and for simplicity we neglect it.

differentiate with respect to c_a

$$2c_{a}\tilde{E} + \left(c_{a}^{2} + c_{b}^{2}\right)\frac{\partial\tilde{E}}{\partial c_{a}} = 2\alpha c_{a} + 2\beta c_{b}$$

At the minimum, $\partial \tilde{E} / \partial c_a = 0$, so this becomes

$$\left(\alpha - \tilde{E}\right)c_a + \beta c_b = 0$$

They have a non-trivial solution (i.e., other than $c_a = cb = 0$) only if the determinant of the coefficients (the *secular determinant*) is zero:

$$\begin{vmatrix} \alpha - \tilde{E} & \beta \\ \beta & \alpha - \tilde{E} \end{vmatrix} = 0$$
$$\left(\alpha - \tilde{E} \right)^2 - \beta^2 = 0$$
$$\tilde{E} = \alpha \pm \beta$$

[Recall the condition for non-trivial solutions: Given the matrix equation Ax = 0, we can multiply by A^{-1} , if it exists, to get $A^{-1}Ax = x =$ 0. So for non-trivial solutions A^{-1} must not exist, i.e. A must be singular, with det(A) = 0.] When $\tilde{E} = \alpha + \beta$ we find $c_a = c_b$, and if the wavefunction is to be normalized (i.e., $c_a^2 = c_b^2 = 1$) we need $c_a = c_b = \sqrt{1/2}$. In the same way, $\tilde{E} = \alpha - \beta$ leads to $c_a = -c_b = \sqrt{1/2}$.

Remember that β is negative.



Molecular orbitals of lithium hydride

Often we need to deal with heteronuclear molecules, of which LiH is the simplest example. Here the two valence orbitals, Li 2s and H 1s, have different energies

$$\alpha_a = \int s_a H s_a d\tau, \qquad \alpha_b = \int s_b H s_b d\tau$$

The secular equations become

$$\begin{pmatrix} \alpha_a - \tilde{E} \end{pmatrix} c_a + \beta c_b = 0 \\ \beta c_a + (\alpha_b - \tilde{E}) c_b = 0 \\ \begin{pmatrix} \alpha_a - \tilde{E} & \beta \\ \beta & \alpha_b - \tilde{E} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

$$\begin{pmatrix} \alpha_a - \tilde{E} & \beta \\ \beta & \alpha_b - \tilde{E} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0 0 = \begin{vmatrix} \alpha_a - \tilde{E} & \beta \\ \beta & \alpha_b - \tilde{E} \end{vmatrix} = (\alpha_a - \tilde{E})(\alpha_b - \tilde{E}) - \beta^2 = \tilde{E}^2 - (\alpha_a + \alpha_b)\tilde{E} + \alpha_a \alpha_b - \beta^2$$

$$\tilde{E} = \frac{1}{2} \left(\alpha_a + \alpha_b \right) \pm \frac{1}{2} \sqrt{\left(\alpha_a - \alpha_b \right)^2 + 4\beta^2}$$

In general, we find the orbital coefficients, c_a and c_b in this case, by substituting the energy back into the secular equations and solving for the coefficients.

The essential features of the orbital coefficients are that if $\alpha_a > \alpha_b$,

- the bonding orbital has |cb| > |ca| and the antibonding orbital has |cb| < |ca|.
- The coefficients have the same sign for the bonding orbital, and opposite signs for the antibonding one.



We can deduce some general results from the energy expression:

- If $\alpha_a = \alpha_b = \alpha$ we get energies $E = \alpha \pm \beta$ as before.
- If $\beta = 0$ there is no interaction and the energies are $E = \alpha_a$ and $E = \alpha_b$.

• For a fixed value of β , the bonding orbital is stabilized most when $\alpha_a - \alpha_b = 0$. If $\alpha_a > \alpha_b$ the stabilization is



$$\tilde{E} = \frac{1}{2} (\alpha_a + \alpha_b) \pm \frac{1}{2} \sqrt{(\alpha_a - \alpha_b)^2 + 4\beta^2}$$

If $|\alpha_a - \alpha_b| \Box \beta$ $E_1 \approx \alpha_a, E_2 \approx \alpha_b$ If $|\alpha_a - \alpha_b| = 0$ $E_1 = \alpha_a - |\beta|, E_2 \approx \alpha_b + |\beta|$

The AOs should have comparable energy.

Lithium hydride: a better approach

How do we know that the Li orbital in this molecule is an *sp* hybrid? We allow the 2*s* and $2p_z$ orbitals to contribute independently to the wavefunction, and let the variation principle find the answer.

$$\tilde{\psi} = c_s \varphi_{\text{Li}2s} + c_p \varphi_{\text{Li}2p_z} + c_h \varphi_{\text{H}1s} = c_s s + c_p p + c_h h$$

We have more α s and β s in this problem. In a real calculation the computer would calculate them. For illustration we assume that $\alpha_s = \alpha_p = \alpha$, $\alpha_h = \alpha + \beta$ and $\beta_{sh} = \beta_{ph} = \beta$. β_{sp} is zero by symmetry. The secular equation becomes

$$\begin{bmatrix} \alpha - \tilde{E} & 0 & \beta \\ 0 & \alpha - \tilde{E} & \beta \\ \beta & \beta & \alpha + \beta - \tilde{E} \end{bmatrix} \begin{pmatrix} c_s \\ c_p \\ c_h \end{pmatrix} = 0$$

The usual procedure is to substitute $\alpha - \tilde{E} = x\beta$ in the secular determinant, and factorize β out of each row. This gives a simple cubic equation for x. It is now quite easy to show that $c_s = c_p$ in two of the solutions (giving an *sp* hybrid $\varphi_{\text{Li2s}} + \varphi_{\text{Li2pz}}$) and $c_s = -c_p$ in the other (giving another *sp* hybrid).

The effect of overlap

In solving the secular equations for the hydrogen molecule ion we assumed that the overlap integral $S = \int s_a s_b d\tau$ was negligible. This is in fact a poor approximation. If we don't ignore it, the eq becomes $\tilde{E} = \frac{(c_a^2 + c_b^2)\alpha + 2c_a c_b \beta}{(c_a^2 + c_b^2 + 2c_b c_b^2)} \implies (c_a^2 + c_b^2 + 2c_b c_b c_b^2)\tilde{E} = (c_a^2 + c_b^2)\alpha + 2c_b c_b^2$

$$\tilde{E} = \frac{\left(c_{a} + c_{b}\right)\alpha + 2c_{a}c_{b}\beta}{c_{a}^{2} + c_{b}^{2} + 2c_{a}c_{b}S} \qquad \Longrightarrow \quad \left(c_{a}^{2} + c_{b}^{2} + 2c_{a}c_{b}S\right)\tilde{E} = \left(c_{a}^{2} + c_{b}^{2}\right)\alpha + 2c_{a}c_{b}\beta$$

and the secular equations become

$$\begin{array}{ccc} \alpha - \tilde{E} & \beta - \tilde{E}S \\ \beta - \tilde{E}S & \alpha - \tilde{E} \end{array} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$



Setting the secular determinant to zero gives

$$\left(\alpha - \tilde{E}\right)^2 = \left(\beta - \tilde{E}S\right)^2$$

Setting $\alpha = 0$, so that we are taking \tilde{E} relative to the non-bonding energy α , we get $\tilde{E} = \frac{\beta}{1+S}$ or $-\frac{\beta}{1-S}$ Since S > 0, the strength of the bonding is reduced, while the strength of the antibonding is

increased.

Linear Variation Functions

$$\phi = c_1 f_1 + c_2 f_2 + \dots + c_n f_n = \sum_{j=1}^n c_j f_j$$

A linear variation function is a linear combination of n linearly
independent functions $f_1, f_2, \dots f_n$.

Based on this principle, the parameters are regulated by the minimization routine so as to obtain the wavefunction that corresponds to the minimum energy. This is taken to be the wavefunction that closely approximates the ground state.

$$\int \phi^* \phi d\tau = \sum_{j,k} c_j c_k S_{jk}$$

overlap integral $S_{jk} \equiv \int f_j^* f_k d\tau$
$$\int \phi^* \hat{H} \phi d\tau = \sum_{j,k} c_j c_k \int f_j \hat{H} f_k d\tau = \sum_{j,k} c_j c_k H_{jk}$$

$$W = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} = \frac{\sum_{j=k}^n \sum_{k=1}^n c_j c_k H_{jk}}{\sum_{j=1}^n \sum_{k=1}^n c_j c_k S_{jk}}$$
$$W \sum_{j=k}^n \sum_{k=1}^n c_j c_k S_{jk} = \sum_{j=1}^n \sum_{k=1}^n c_j c_k H_{jk}$$

A necessary condition for a minimum

$$\frac{\partial W}{\partial c_i} = 0, \qquad i = 1, 2, \cdots, n$$

$$\frac{\partial W}{\partial c_i} \sum_{j=1}^n \sum_{k=1}^n c_j c_k S_{jk} + W \frac{\partial}{\partial c_i} \sum_{j=1}^n \sum_{k=1}^n c_j c_k S_{jk}$$
$$= \frac{\partial}{\partial c_i} \sum_{j=1}^n \sum_{k=1}^n c_j c_k H_{jk}, \ i = 1, 2, \cdots, n$$

$$\frac{\partial}{\partial c_i} \sum_{j=1}^n \sum_{k=1}^n c_j c_k S_{jk} = \sum_{j=1}^n \sum_{k=1}^n c_k \delta_{ij} S_{jk} + \sum_{j=1}^n \sum_{k=1}^n c_j \delta_{ik} S_{jk}$$
$$= \sum_{k=1}^n c_k S_{ik} + \sum_{j=1}^n c_j S_{ji}$$
$$= 2\sum_{k=1}^n c_k S_{ik}$$

$$\frac{\partial}{\partial c_i} \sum_{j=1}^n \sum_{k=1}^n c_j c_k H_{jk} = 2 \sum_{k=1}^n c_k H_{ik}$$

$$2W\sum_{k=1}^{n} c_k S_{ik} = 2\sum_{k=1}^{n} c_k H_{ik}, \qquad i = 1, 2, \cdots, n$$

$$(H_{11} - S_{11}W)c_1 + \dots + (H_{1n} - S_{1n}W)c_n = 0$$

$$(H_{n1} - S_{n1}W)c_1 + \dots + (H_{nn} - S_{nn}W)c_n = 0$$

$$\det(H_{ij} - S_{ij}W) = 0$$

$$\begin{vmatrix} H_{11} - S_{11}W & H_{12} - S_{12}W & \cdots & H_{1n} - S_{1n}W \\ H_{21} - S_{21}W & H_{22} - S_{22}W & \cdots & H_{2n} - S_{2n}W \\ \vdots & \vdots & \vdots & \vdots \\ H_{n1} - S_{n1}W & H_{n2} - S_{n2}W & \cdots & H_{nn} - S_{nn}W \end{vmatrix} = 0$$

• From the variation theorem, we know that the lowest value of root is the upper bound for the system's ground-state energy.

• If approximation to the energies of more states are wanted, we add more functions f_k to the trial function ϕ .

• The addition of more functions f_k can be shown to increase the accuracy of the previously calculated energies.