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# Variational Principle Variational Calculations of Energy Eigenstates

Ronald Lovett

*Washington University in St. Louis*

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## Variational Calculations of Energy Eigenstates

ground state wavefunction

### References

*Quantum Chemistry*, D.A. McQuarrie, Chapter 9, Sections 21–24, (Chem QD462 M25).

*Hückel Molecular Orbital Theory*, C.A. Coulson, *et al.*, (Chem QD461 H4).

### General Formulation

An orthonormal basis set  $\{\phi_n\}_{n=1}^{\infty}$  can be used to represent an energy eigenfunction. An *approximate* representation can be generated by using only a *finite* set of vectors,  $\{\phi_n\}_{n=1}^N$ . This moves the space in which eigenvectors are sought from an infinite-dimensional function space to a finite dimensional vector space. In the usual situation, one motivates this approximation with the argument that the subspace spanned by  $\{\phi_n\}_{n=1}^N$  is large enough to accurately describe low-lying energy states. This is particularly plausible if the  $\{\phi_n\}$  correspond to energy eigenstates of a Hamiltonian that is similar to the actual Hamiltonian of interest.

If  $\hat{H}$  is the Hamiltonian of interest, the energy eigenvalue problem

$$\hat{H}\psi = E\psi \quad (1)$$

has the approximate matrix representation

$$\langle \phi_i | \hat{H} \psi \rangle = \sum_{j=1}^N \langle \phi_i | \hat{H} \phi_j \rangle \langle \phi_j | \psi \rangle = E \langle \phi_i | \psi \rangle \quad i = 1, \dots, N.$$

If the expansion coefficients,  $c_i = \langle \phi_i | \psi \rangle$ ,  $i = 1, \dots, N$ , are interpreted as the components of an  $N$ -dimensional vector and the

$$H_{ij} = \langle \phi_i | \hat{H} \phi_j \rangle = H_{ji}^* \quad 1 \leq i, j \leq N$$

are interpreted as the matrix elements of an  $N \times N$  array  $\mathcal{H}$ , (1) is equivalent to the matrix equation

$$\mathcal{H} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix}, \quad (2)$$

or the set of  $N$  equations

$$\sum_{j=1}^N H_{ij} c_j = E c_i, \quad i = 1, \dots, N. \quad (3)$$

Equations (2) or (3) give an  $N$ -dimensional eigenvector problem that *approximates* the original problem (1). The eigenvectors and eigenvalues of (2) or (3) will only be approximations to those of the original problem.

### The Variational Principle

Another argument is often given for (2) or (3). Since any state has a representation

$$\psi = \sum_{n=0}^{\infty} \langle \chi_n | \psi \rangle \chi_n$$

in terms of the energy eigenvectors  $\{\chi_n\}_{n=0}^{\infty}$ , the *expectation* of the energy in state  $\psi$  can be written

$$\begin{aligned} \langle \psi | \hat{H} \psi \rangle &= \sum_{n=0}^{\infty} |\langle \chi_n | \psi \rangle|^2 E_n \\ &= E_0 \sum_{n=0}^{\infty} |\langle \chi_n | \psi \rangle|^2 + \sum_{n=0}^{\infty} |\langle \chi_n | \psi \rangle|^2 (E_n - E_0) \\ &= E_0 + \sum_{n=0}^{\infty} |\langle \chi_n | \psi \rangle|^2 (E_n - E_0). \end{aligned}$$

Since all the terms in the last sum are  $\geq 0$ ,

$$\langle \psi | \hat{H} \psi \rangle \geq E_0 \quad (4)$$

for all *normalized*  $\psi$ .

If we now consider states that can be represented in terms of a *finite* set of orthonormal vectors  $\{\phi_n\}_{n=1}^N$ , i.e., states of the form

$$\psi = \sum_{n=1}^N (a_n + ib_n) \phi_n \quad (5)$$

with  $a_n$  and  $b_n$  real numbers, then (4) shows that the numbers  $\{a_n, b_n\}_{n=1}^N$  that minimize the expectation of  $\hat{H}$  produce the best estimate for the ground state energy. The

*variational principle* asserts that the best approximation to the ground state eigenvector among the vectors in the  $N$ -dimensional subspace (5) is that that minimizes  $\langle \psi | \hat{H} \psi \rangle$ .

The chief complexity in finding this state arises from the fact that we must consider only normalized states. For these,

$$1 = \langle \psi | \psi \rangle = \sum_{n=1}^N [a_n^2 + b_n^2]. \quad (6)$$

Not all the  $\{a_n, b_n\}$  are independent. If (6) is used to fix  $b_N$  in terms of the remaining  $2N - 1$  coefficients, then the remaining coefficients are fixed by the  $2N - 1$  relations

$$\begin{aligned} 0 &= \frac{\partial}{\partial a_j} \langle \psi | \hat{H} \psi \rangle \\ &= \langle \frac{\partial \psi}{\partial a_j} | \hat{H} \psi \rangle + \langle \psi | \hat{H} \frac{\partial \psi}{\partial a_j} \rangle \\ &= \langle \phi_j + i\phi_N \frac{\partial b_N}{\partial a_j} | \hat{H} \psi \rangle + \langle \psi | \hat{H} (\phi_j + i\phi_N \frac{\partial b_N}{\partial a_j}) \rangle \\ &= \langle \phi_j | \hat{H} \psi \rangle + \langle \psi | \hat{H} \phi_j \rangle + \frac{ia_j}{b_N} (\langle \phi_N | \hat{H} \psi \rangle - \langle \psi | \hat{H} \phi_N \rangle), \quad j = 1, \dots, N, \end{aligned} \quad (7)$$

and

$$\begin{aligned} 0 &= \frac{\partial}{\partial b_j} \langle \psi | \hat{H} \psi \rangle \\ &= \langle i\phi_j + i\phi_N \frac{\partial b_N}{\partial b_j} | \hat{H} \psi \rangle + \langle \psi | \hat{H} (i\phi_j + i\phi_N \frac{\partial b_N}{\partial b_j}) \rangle \\ &= -i(\langle \phi_j | \hat{H} \psi \rangle - \langle \psi | \hat{H} \phi_j \rangle) + i\frac{b_j}{b_N} (\langle \phi_N | \hat{H} \psi \rangle - \langle \psi | \hat{H} \phi_N \rangle), \quad j = 1, \dots, N-1. \end{aligned} \quad (8)$$

If we set

$$\lambda = \frac{1}{2ib_N} (\langle \phi_N | \hat{H} \psi \rangle - \langle \psi | \hat{H} \phi_N \rangle), \quad (9)$$

then all these relations are equivalent to

$$\lambda = \frac{\langle \phi_j | \hat{H} \psi \rangle - \langle \psi | \hat{H} \phi_j \rangle}{2ib_j} = \frac{\langle \phi_j | \hat{H} \psi \rangle + \langle \psi | \hat{H} \phi_j \rangle}{2a_j}, \quad j = 1, \dots, N. \quad (10)$$

These relations can be rearranged to

$$\begin{aligned}\langle \phi_j | \hat{H} \psi \rangle - \langle \psi | \hat{H} \phi_j \rangle &= 2ib_j \lambda, \\ \langle \phi_j | \hat{H} \psi \rangle + \langle \psi | \hat{H} \phi_j \rangle &= 2a_j \lambda.\end{aligned}\tag{11}$$

The average of the two relations in (11) gives

$$\langle \phi_j | \hat{H} \psi \rangle = (a_j + ib_j) \lambda = \lambda \langle \phi_j | \psi \rangle$$

for all  $j$ . That is,

$$\sum_{k=1}^N \langle \phi_j | \hat{H} \phi_k \rangle \langle \phi_k | \psi \rangle = \lambda \langle \phi_j | \psi \rangle.\tag{12}$$

But these are just (2) and (3) with  $\lambda = E$ . The correct  $E_0$  will lie *below* the lowest eigenvalue  $\lambda$  associated with (12).

## The Hückel Molecular Orbital Theory

“The Hückel molecular-orbital method (or HMO method) is probably the most widely used of all quantum-chemical computational schemes. It is based on a series of assumptions, of which many are arbitrary. It is patterned on quantum mechanics, but it is really no more than a useful empirical scheme that rationalizes much chemical experience concerning  $\pi$ -electron molecules.”

As the “ $\pi$ -electrons” in a molecule are less tightly bound than the remaining electrons, they may be approximated as electrons moving independently in a field provided by the remaining charges in the molecule. If there are  $N$  atoms in a molecule that contribute a  $2p_z$  orbital to the  $\pi$ -system, the  $\pi$ -electron states may be pictured as linear combinations of “atomic orbitals,”

$$\psi = \sum_{n=1}^N c_n \phi_n.$$

The  $\phi_n$  are “pictured” as  $2p_z$  orbitals, but more realistically they are energy eigenstates of an electron moving in the field of the remaining charges of the molecule localized at atom  $n$ .

The realization by Hückel of a molecular orbital picture is actually independent of what the  $\phi_n$  are. It is simply *assumed* that there is an orthonormal basis set  $\{\phi_n\}_{n=1}^N$  in which the matrix elements of  $\hat{H}$  are

$$H_{ij} = \begin{cases} \alpha & \text{if } i = j, \\ \beta & \text{if } (i, j) \text{ are neighbors,} \\ 0 & \text{otherwise.} \end{cases}$$

Here " $\alpha$ " is the energy of an electron in an isolated  $\phi_n$  state and " $\beta$ " is an energy contribution arising from the attraction of neighboring states for an electron. If a free electron has energy = 0, then  $\alpha, \beta < 0$ .

As an example, consider cyclobutadiene. If  $\phi_1, \dots, \phi_4$  are the local ' $2p_z$ ' orbitals encountered as one moves around the ring, then the HMO Hamiltonian for the  $\pi$  electrons in this basis set is

$$H = \begin{bmatrix} \alpha & \beta & 0 & \beta \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ \beta & 0 & \beta & \alpha \end{bmatrix}.$$

The energy eigenvalues are (in ascending order)  $\alpha + 2\beta, \alpha, \alpha, \alpha - 2\beta$ . The ground state has two electrons with energy  $\alpha + 2\beta$  and two with energy  $\alpha$ . Spectroscopic excitation requires energy  $2|\beta|$ . Using HMO theory as an empirical fitting scheme, one finds good prediction of the first absorption of the  $\pi$ -system with

$$\beta = -2.71\text{eV or } -21,900\text{cm}^{-1}$$

Basis Set





## Problem Set #5

1. Let

$$m = \begin{bmatrix} a & b & 0 \\ b & a & b \\ 0 & b & a \end{bmatrix}.$$

In *Mathematica*  $m$  is represented as a list of lists,  $m = \{\{a,b,0\},\{b,a,b\},\{0,b,a\}\}$ . `MatrixForm[m]` will display  $m$  (if the screen is large enough) in standard form.

Determine the eigenvalues and eigenvectors of  $m$ .

`Eigenvalues[m]` returns a list of eigenvalues. `Eigenvectors[m]` returns a list of eigenvectors.

Construct an orthonormal basis set out of the eigenvectors. If this *set* of (orthonormal) vectors is turned into a matrix  $T = \{v_1, v_2, v_3\}$  and  $\tilde{T}$  is the transpose of  $T$  ( $\tilde{T}_{ij} = T_{ji}$ ), what is the matrix  $T \cdot \tilde{T}$ ? What is  $T \cdot m \cdot \tilde{T}$ ?

`Transpose[T]` returns the 'transposed' array. If A and B are two matrices, A.B gives the matrix product of A and B.

2. In the double well problem, the bound state eigenvectors decay exponentially outside the well. The *shifted* well

$$V(x) = \begin{cases} 0, & 0 \leq x < 3, \\ -1, & 3 \leq x \leq 8.5, \\ 0, & 8.5 < x < 9.5, \\ -1, & 9.5 \leq x \leq 15, \\ 0, & 15 < x \leq 18, \end{cases} \quad (1)$$

is rather close to  $V(x) = -1$  for  $0 \leq x \leq 18$ , so it is a reasonable approximation that the eigenvectors are close to the eigenvectors of a particle in a  $0 \leq x \leq 18$  box. Give the matrix representation for the Hamiltonian for the double well (1) in this basis set using the first ten particle-in-a-box states. What are the six lowest eigenvalues? Repeat this with a 20 dimensional basis set. To show how the quality of the representation of the first six



states changes as the size of the basis set is increased, make a plot that shows the first six eigenvalues in these two approximations and in the real problem. Similarly, make plots that show how close the two lowest energy eigenfunctions come to the correct eigenfunctions.

3. Consider the double well problem again, but now suppose that an additional interaction with an external electric field is present, i.e., that

$$\hat{H} = \hat{H}_{double\_well} + \hat{V}_{electrical}.$$

Take

$$\hat{V}_{electrical} = -qE(x - x_{center}),$$

with  $E$  the magnitude of the component of the electric field along the  $x$ -axis and  $q$  the charge of the particle located at  $x$ , and a neutralizing charge at  $x_{center}$ . Make a  $2 \times 2$  matrix representation for the Hamiltonian using the two lowest eigenvectors of  $\hat{H}_{double\_well}$ . Determine the eigenvalues of  $\hat{H}$ . Make a plot of these as a function of  $qE$  in  $0 \leq qE \leq 0.02$ .

4. Show that a shift in the zero of energy can remove the “ $\alpha$ ” of HMO theory. Is  $\alpha$  observable?
5. Determine the energy eigenvalues for the HMO representation of the  $\pi$ -electrons in the cyclic molecules  $C_4H_4$ ,  $C_6H_6$ ,  $C_8H_8$ , and  $C_{10}H_{10}$ . Identify the molecular orbitals that are occupied in the ground states of these molecules and make a sketch of what these orbitals look like. What is the contribution of the  $\pi$ -electrons to molecular binding in these molecules?