

2.1: The Variational Method

For the kind of potentials that arise in atomic and molecular structure, the Hamiltonian H is a Hermitian operator that is bounded from below (i.e., it has a lowest eigenvalue). Because it is Hermitian, it possesses a complete set of orthonormal eigenfunctions $\{|\psi_j\rangle\}$. Any function Φ that depends on the same spatial and spin variables on which H operates and obeys the same boundary conditions that the $\{\Psi_j\}$ obey can be expanded in this complete set

$$\Phi = \sum_j C_j |\psi_j\rangle.$$

The expectation value of the Hamiltonian for any such function can be expressed in terms of its C_j coefficients and the **exact** energy levels E_j of H as follows:

$$\langle \Phi | H | \Phi \rangle = \sum_{ij} C_i C_j \langle \psi_i | H | \psi_j \rangle = \sum_j |C_j|^2 E_j.$$

If the function Φ is normalized, the sum $\sum_j |C_j|^2$ is equal to unity. Because H is bounded from below, all of the E_j must be greater than or equal to the lowest energy E_0 . Combining the latter two observations allows the energy expectation value of Φ to be used to produce a very important inequality:

$$\langle \Phi | H | \Phi \rangle \geq E_0.$$

The equality can hold only if Φ is equal to ψ_0 ; if Φ contains components along any of the other ψ_j , the energy of Φ will exceed E_0 .

This upper-bound property forms the basis of the so-called **variational method** in which 'trial wavefunctions' Φ are constructed:

1. To guarantee that Φ obeys all of the boundary conditions that the exact Ψ_j do and that Φ is of the proper spin and space symmetry and is a function of the same spatial and spin coordinates as the Ψ_j ;
2. With parameters embedded in Φ whose 'optimal' values are to be determined by making $\langle \Phi | H | \Phi \rangle$ a minimum.

It is perfectly acceptable to vary any parameters in Φ to attain the lowest possible value for $\langle \Phi | H | \Phi \rangle$ because the proof outlined above constrains this expectation value to be above the true lowest eigenstate's energy E_0 for **any** Φ . The philosophy then is that the Φ that gives the lowest $\langle \Phi | H | \Phi \rangle$ is the best because its expectation value is closest to the exact energy.

Linear Variational Calculations

Quite often a **trial wavefunction** is expanded as a linear combination of other functions (not the eigenvalues of the Hamiltonian, since they are not known)

$$\Phi = \sum_J^N C_J |\Phi_J\rangle. \quad (2.1.1)$$

In these cases, one says that a 'linear variational' calculation is being performed. The set of functions $\{\Phi_J\}$ are usually constructed to obey all of the boundary conditions that the exact state Ψ obeys, to be functions of the the same coordinates as Ψ , and to be of the same spatial and spin symmetry as Ψ . Beyond these conditions, the $\{\Phi_J\}$ are nothing more than members of a set of functions that are convenient to deal with (e.g., convenient to evaluate Hamiltonian matrix elements $\langle \Phi_I | H | \Phi_J \rangle$ that can, in principle, be made complete if more and more such functions are included in the expansion in Equation 2.1.1 (i.e., increase N).

For such a trial wavefunction, the energy depends quadratically on the 'linear variational' C_J coefficients:

$$\langle \Phi | H | \Phi \rangle = \sum_{I,J}^{N,N} C_I C_J \langle \Phi_I | H | \Phi_J \rangle.$$

Minimization of this energy with the constraint that Φ remain normalized, i.e.,

$$\langle \Phi | \Phi \rangle = \sum_{IJ} C_I C_J \langle \Phi_I | \Phi_J \rangle = 1$$

gives rise to a so-called **secular** or **eigenvalue-eigenvector** problem:

$$\sum_J [\langle \Phi_I | H | \Phi_J \rangle - E \langle \Phi_I | \Phi_J \rangle] C_J = \sum_J [H_{IJ} - E S_{IJ}] C_J = 0.$$

If the functions $\{|\Phi_J\rangle\}$ are orthonormal, then the overlap matrix S reduces to the unit matrix and the above generalized eigenvalue problem reduces to the more familiar form:

$$\sum_J^N H_{IJ} C_J = E C_I.$$

The secular problem, in either form, has as many eigenvalues E_i and eigenvectors $\{C_{iJ}\}$ as the dimension of the H_{IJ} matrix as Φ . It can also be shown that between successive pairs of the eigenvalues obtained by solving the secular problem at least one exact eigenvalue must occur (i.e., $E_{i+1} > E_{exact} > E_i$, for all i). This observation is referred to as 'the bracketing theorem'.

Variational methods, in particular the linear variational method, are the most widely used approximation techniques in quantum chemistry. To implement such a method one needs to know the Hamiltonian H whose energy levels are sought and one needs to construct a trial wavefunction in which some 'flexibility' exists (e.g., as in the linear variational method where the C_J coefficients can be varied). In Section 6 this tool will be used to develop several of the most commonly used and powerful molecular orbital methods in chemistry.

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