Chapter 2

Approximation Methods Can be Used When Exact Solutions to the Schrödinger Equation Can Not be Found.

In applying quantum mechanics to 'real' chemical problems, one is usually faced with a Schrödinger differential equation for which, to date, no one has found an analytical solution. This is equally true for electronic and nuclear-motion problems. It has therefore proven essential to develop and efficiently implement mathematical methods which can provide approximate solutions to such eigenvalue equations. Two methods are widely used in this context- the variational method and perturbation theory. These tools, whose use permeates virtually all areas of theoretical chemistry, are briefly outlined here, and the details of perturbation theory are amplified in Appendix D.

I. 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 $\{\psi_j\}$. 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

$$\Phi = \Sigma_j \; C_j \; \psi_j.$$

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:

$$\langle\Phi|H|\Phi\rangle = \Sigma_{ij} \; C_i C_j \; \langle\psi_i|H|\psi_j\rangle = \Sigma_j |C_j|^2 \; E_j.$$

If the function Φ is normalized, the sum $\Sigma_j \; |C_j|^2$ 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:

i. 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;

ii. 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 closes to the exact energy.

Quite often a trial wavefunction is expanded as a linear combination of other functions

$$\Phi = \Sigma_J C_J \Phi_J.$$

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 $\langle\Phi_I|H|\Phi_J\rangle$) and that can, in principle, be made complete if more and more such functions are included.

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

$$\langle\Phi|H|\Phi\rangle = \Sigma_{IJ} C_I C_J \langle\Phi_I|H|\Phi_J\rangle.$$

Minimization of this energy with the constraint that Φ remain normalized ($\langle\Phi|\Phi\rangle = 1 = \Sigma_{IJ} C_I C_J \langle\Phi_I|\Phi_J\rangle$) gives rise to a so-called secular or eigenvalue-eigenvector problem:

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

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

$$\Sigma_J H_{IJ} C_J = E C_I.$$

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.

II. Perturbation Theory

[Suggested Extra Reading- Appendix D; Time Independent Perturbation Theory]

Perturbation theory is the second most widely used approximation method in quantum chemistry. It allows one to estimate the splittings and shifts in energy levels and changes in wavefunctions that occur when an external field (e.g., an electric or magnetic field or a field that is due to a surrounding set of 'ligands'- a crystal field) or a field arising when a previously-ignored term in the Hamiltonian is applied to a species whose 'unperturbed' states are known. These 'perturbations' in energies and wavefunctions are expressed in terms of the (complete) set of unperturbed eigenstates.

Assuming that <u>all</u> of the wavefunctions Φ_k and energies E_k^0 belonging to the unperturbed Hamiltonian H^0 are known

$$H^0 \Phi_k = E_k^0 \Phi_k ,$$

and given that one wishes to find eigenstates (ψ_k and E_k) of the perturbed Hamiltonian

$$H=H^0+\lambda V,$$

perturbation theory expresses ψ_k and E_k as power series in the perturbation strength λ:

$$\psi_k = \sum_{n=0}^{\infty} \lambda^n \psi_k^{(n)}$$

$$E_k = \sum_{n=0}^{\infty} \lambda^n E_k^{(n)} .$$

The systematic development of the equations needed to determine the $E_k^{(n)}$ and the $\psi_k^{(n)}$ is presented in Appendix D. Here, we simply quote the few lowest-order results.

The zeroth-order wavefunctions and energies are given in terms of the solutions of the unperturbed problem as follows:

$$\psi_k^{(0)} = \Phi_k \text{ and } E_k^{(0)} = E_k^0.$$

This simply means that one must be willing to identify one of the unperturbed states as the 'best' approximation to the state being sought. This, of course, implies that one must therefore strive to find an unperturbed model problem, characterized by H^0 that represents the true system as accurately as possible, so that one of the Φ_k will be as close as possible to ψ_k.

The first-order energy correction is given in terms of the zeroth-order (i.e., unperturbed) wavefunction as:

$$E_k^{(1)} = \langle \Phi_k | V | \Phi_k \rangle,$$

which is identified as the average value of the perturbation taken with respect to the unperturbed function Φ_k. The so-called first-order wavefunction $\psi_k^{(1)}$ expressed in terms of the complete set of unperturbed functions $\{\Phi_J\}$ is:

$$\psi_k^{(1)} = \sum_{j \neq k} \langle \Phi_j | V | \Phi_k \rangle / [E_k^0 - E_j^0] \; | \Phi_j \rangle .$$

The second-order energy correction is expressed as follows:

$$E_k^{(2)} = \sum_{j \neq k} |\langle \Phi_j | V | \Phi_k \rangle|^2 / [E_k^0 - E_j^0] \ ,$$

and the second-order correction to the wavefunction is expressed as

$$\psi_k^{(2)} = \Sigma_{j \neq k} [E_k^0 - E_j^0]^{-1} \Sigma_{l \neq k} \{ \langle \Phi_j | V | \Phi_l \rangle - \delta_{j,l} E_k^{(1)} \}$$

$$\langle \Phi_l | V | \Phi_k \rangle [E_k^0 - E_l^0]^{-1} | \Phi_j \rangle .$$

An essential point about perturbation theory is that the energy corrections $E_k^{(n)}$ and wavefunction corrections $\psi_k^{(n)}$ are expressed in terms of integrals over the unperturbed wavefunctions Φ_k involving the perturbation (i.e., $\langle \Phi_j | V | \Phi_l \rangle$) and the unperturbed energies E_j^0. Perturbation theory is most useful when one has, in hand, the solutions to an unperturbed Schrödinger equation that is reasonably 'close' to the full Schrödinger equation whose solutions are being sought. In such a case, it is likely that low-order corrections will be adequate to describe the energies and wavefunctions of the full problem.

It is important to stress that although the solutions to the full 'perturbed' Schrödinger equation are expressed, as above, in terms of sums over all states of the unperturbed Schrödinger equation, it is improper to speak of the perturbation as creating excited-state species. For example, the polarization of the 1s orbital of the Hydrogen atom caused by the application of a static external electric field of strength *E* along the z-axis is described, in first-order perturbation theory, through the sum

$$\Sigma_{n=2,\infty} \ \varphi_{np_0} \langle \varphi_{np_0} | E \, e \, r \cos\theta | 1s \rangle [E_{1s} - E_{np_0}]^{-1}$$

over all $p_z = p_0$ orbitals labeled by principal quantum number n. The coefficient multiplying each p_0 orbital depends on the energy gap corresponding to the 1s-to-np 'excitation' as well as the electric dipole integral $\langle \varphi_{np_0} | E \, e r \cos\theta | 1s \rangle$ between the 1s orbital and the np_0 orbital.

This sum describes the polarization of the 1s orbital in terms of functions that have p_0 symmetry; by combining an s orbital and p_0 orbitals, one can form a 'hybrid-like' orbital that is nothing but a distorted 1s orbital. The appearance of the excited np_0 orbitals has

nothing to do with forming excited states; these np_0 orbitals simply provide a set of functions that can describe the response of the 1s orbital to the applied electric field.

The relative strengths and weaknesses of perturbation theory and the variational method, as applied to studies of the electronic structure of atoms and molecules, are discussed in Section 6.