2.2: 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 all 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:

$$\psi_k^{(0)} = \Phi_k$$

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:

$$E_k^{(1)} = <\Phi_k|V|\Phi_k>,$$

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:

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

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

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

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

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

$$\sum_{n=2,\infty} \phi_{np_0} \frac{\langle \phi_{np_0} | E \text{ e r } \cos\theta | 1s \rangle}{E_{1s} - E_{np_0}}$$

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 $\langle \phi_{np_0} | E \text{ e r } \cos\theta | 1s \rangle$ 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.