

Time Independent Perturbation Theory D

Perturbation theory is used in two qualitatively different contexts in quantum chemistry. It allows one to estimate (because perturbation theory is usually employed through some finite order and may not even converge if extended to infinite order) the splittings and shifts in energy levels and changes in wavefunctions that occur when an external field (e.g., electric or magnetic or that due to a surrounding set of 'ligands'- a crystal field) is applied to an atom, molecule, ion, or solid whose 'unperturbed' states are known. These 'perturbations' in energies and wavefunctions are expressed in terms of the (complete) set of unperturbed states. For example, the distortion of the 2s orbital of a Li atom due to the application of an external electric field along the y-axis is described by adding to the (unperturbed) 2s orbital components of p_y-type orbitals (2p, 3p, etc.):

$$= a 2s + \sum_n C_n n p_y.$$

The effect of adding in the p_y orbitals is to polarize the 2s orbital along the y-axis. The amplitudes C_n are determined via the equations of perturbation theory developed below; the change in the energy of the 2s orbital caused by the application of the field is expressed in terms of the C_n coefficients and the (unperturbed) energies of the 2s and n p_y orbitals.

There is another manner in which perturbation theory is used in quantum chemistry that does not involve an externally applied perturbation. Quite often one is faced with solving a Schrödinger equation to which no exact solution has been (yet) or can be found. In such cases, one often develops a 'model' Schrödinger equation which in some sense is designed to represent the system whose full Schrödinger equation can not be solved. The difference between the Hamiltonia of the full and model problems, H and H⁰, respectively is used to define a perturbation V=H-H⁰. Perturbation theory is then employed to approximate the energy levels and wavefunctions of the full H in terms of the energy levels and wavefunctions of the model system (which, by assumption, can be found). The 'imperfection' in the model problem is therefore used as the perturbation. The success of such an approach depends strongly on how well the model H⁰ represents the true problem (i.e., on how 'small' V is). For this reason, much effort is often needed to develop approximate Hamiltonia for which V is small and for which the eigenfunctions and energy levels can be found.

I. Structure of Time-Independent Perturbation Theory

A. The Power Series Expansions of the Wavefunction and Energy

Assuming that all wavefunctions ψ_k and energies E_k^0 belonging to the unperturbed Hamiltonian H^0 are known

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

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

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

perturbation theory begins by expressing ψ_k and E_k as power series in the perturbation strength λ :

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

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

Moreover, it is assumed that, as the strength of the perturbation is reduced to zero, ψ_k reduces to one of the unperturbed states ψ_k^0 and that the full content of ψ_k in ψ_k^0 is contained in the first term $\psi_k^{(0)}$.

This means that $\psi_k^{(0)} = \psi_k^0$ and $E_k^{(0)} = E_k^0$, and so

$$\psi_k = \psi_k^0 + \sum_{n=1}^{\infty} \lambda^n \psi_k^{(n)} = \psi_k^0 + \psi_k'$$

$$E_k = E_k^0 + \sum_{n=1}^{\infty} \lambda^n E_k^{(n)} = E_k^0 + E_k'.$$

In the above expressions, λ would be proportional to the strength of the electric or magnetic field if one is dealing with an external-field case. When dealing with the situation for which V is the imperfection in the model H^0 , λ is equal to unity; in this case, one thinks of formulating and solving for the perturbation expansion for variable λ after which λ is set equal to unity.

B. The Order-by-Order Energy Equations

Equations for the order-by-order corrections to the wavefunctions and energies are obtained by using these power series expressions in the full Schrödinger equation:

$$(H - E_k) \psi_k = 0.$$

Multiplying through by ψ_k^* and integrating gives the expression in terms of which the total energy is obtained:

$$\langle \psi_k | H | \psi_k \rangle = E_k \langle \psi_k | \psi_k \rangle = E_k.$$

Using the fact that ψ_k^0 is an eigenfunction of H^0 and employing the power series expansion of ψ_k allows one to generate the fundamental relationships among the energies $E_k^{(n)}$ and the wavefunctions $\psi_k^{(n)}$:

$$E_k = \langle \psi_k | H^0 | \psi_k \rangle + \langle \psi_k | V | \psi_k \rangle = E_k^0 + \langle \psi_k | V | \sum_{n=0}^{\infty} \lambda^n \psi_k^{(n)} \rangle.$$

The lowest few orders in this expansion read as follows:

$$E_k = E_k^0 + \langle \psi_k^0 | V | \psi_k^0 \rangle + 2 \langle \psi_k^0 | V | \psi_k^{(1)} \rangle + 3 \langle \psi_k^0 | V | \psi_k^{(2)} \rangle + \dots$$

If the various $\psi_k^{(n)}$ can be found, then this equation can be used to compute the order-by-order energy expansion.

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

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

the average value of the perturbation taken over ψ_k .

C. The Order-by-Order Wavefunction Equations

To obtain workable expressions for the perturbative corrections to the wavefunction ψ_k , the full Schrödinger equation is first projected against all of the unperturbed eigenstates $\{ | \psi_j \rangle \}$ other than the state ψ_k whose perturbative corrections are sought:

$$\langle \psi_j | H | \psi_k \rangle = E_k \langle \psi_j | \psi_k \rangle, \text{ or}$$

$$\langle \psi_j | H^0 | \psi_k \rangle + \langle \psi_j | V | \psi_k \rangle = E_k \langle \psi_j | \psi_k \rangle, \text{ or}$$

$$\langle \psi_j | \psi_k \rangle E_j^0 + \langle \psi_j | V | \psi_k \rangle = E_k \langle \psi_j | \psi_k \rangle, \text{ or finally}$$

$$\langle \psi_j | V | \psi_k \rangle = [E_k - E_j^0] \langle \psi_j | \psi_k \rangle.$$

Next, each component $\psi_k^{(n)}$ of the eigenstate ψ_k is expanded in terms of the unperturbed eigenstates (as they can be because the $\{ \psi_k \}$ form a complete set of functions):

$$\psi_k = \psi_k + \sum_{j \neq k, n=1}^{\infty} c_{j,n} \langle \psi_j | \psi_k^{(n)} \rangle | \psi_j \rangle.$$

Substituting this expansion for ψ_k into the preceding equation gives

$$\langle \psi_j | V | \psi_k \rangle + \sum_{n=1}^{\infty} c_{j,n} \langle \psi_j | \psi_k^{(n)} \rangle \langle \psi_j | V | \psi_k \rangle$$

$$= [E_k - E_j^0] \sum_{n=1}^{\infty} c_{j,n} \langle \psi_j | \psi_k^{(n)} \rangle.$$

To extract from this set of coupled equations relations that can be solved for the coefficients $\langle \psi_j | \psi_k^{(n)} \rangle$, which embodies the desired wavefunction perturbations $\psi_k^{(n)}$, one collects together all terms with like power of λ in the above general equation (in doing so, it is important to keep in mind that E_k itself is given as a power series in λ).

The λ^0 terms vanish, and the first-order terms reduce to:

$$\langle \psi_j | V | \psi_k \rangle = [E_k^0 - E_j^0] \langle \psi_j | \psi_k^{(1)} \rangle,$$

which can be solved for the expansion coefficients of the so-called first-order wavefunction $\psi_k^{(1)}$:

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

When this result is used in the earlier expression for the second-order energy correction, one obtains:

$$E_k^{(2)} = \sum_j \langle j | V | k \rangle^2 / [E_k^0 - E_j^0] .$$

The terms proportional to $\psi_k^{(2)}$ are as follows:

$$\begin{aligned} \langle 1 | k \rangle \langle 1 | \psi_k^{(1)} \rangle &= \langle j | V | 1 \rangle \\ &= [E_k^0 - E_j^0] \langle j | \psi_k^{(2)} \rangle + E_k^{(1)} \langle j | \psi_k^{(1)} \rangle . \end{aligned}$$

The solution to this equation can be written as:

$$\langle j | \psi_k^{(2)} \rangle = [E_k^0 - E_j^0]^{-1} \langle 1 | k \rangle \langle 1 | \psi_k^{(1)} \rangle \{ \langle j | V | 1 \rangle - \sum_l E_k^{(1)} \} .$$

Because the expansion coefficients $\langle 1 | \psi_k^{(1)} \rangle$ of $\psi_k^{(1)}$ are already known, they can be used to finally express the expansion coefficients of $\psi_k^{(2)}$ totally in terms of zeroth-order quantities:

$$\begin{aligned} \langle j | \psi_k^{(2)} \rangle &= [E_k^0 - E_j^0]^{-1} \langle 1 | k \rangle \{ \langle j | V | 1 \rangle - \sum_l E_k^{(1)} \} \\ &\langle 1 | V | k \rangle [E_k^0 - E_l^0]^{-1} , \end{aligned}$$

which then gives

$$\begin{aligned} \psi_k^{(2)} &= \sum_j \langle j | \psi_k^{(2)} \rangle | j \rangle \\ &= \sum_j \langle j | V | k \rangle [E_k^0 - E_l^0]^{-1} | j \rangle . \end{aligned}$$

D. Summary

An essential thing to stress concerning the above development of so-called Rayleigh-Schrödinger perturbation theory (RSPT) is that each of the energy corrections $E_k^{(n)}$ and wavefunction corrections $\psi_k^{(n)}$ are expressed in terms of integrals over the unperturbed wavefunctions ψ_k involving the perturbation (i.e., $\langle j | V | 1 \rangle$) and the unperturbed energies E_j^0 . As such, these corrections can be symmetry-analyzed to determine, for example, whether perturbations of a given symmetry will or will not affect particular states. For example, if the state under study belongs to a non-degenerate representation in the absence of the perturbation V , then its first-order energy correction $\langle k | V | k \rangle$ will be non-zero only if V contains a totally symmetric component (because the direct product of the symmetry of ψ_k with itself is the totally symmetric representation). Such an analysis predicts, for example, that the energy of an s orbital of an atom will be unchanged, in first-order, by the application of an external electric field because the perturbation

$$V = e \mathbf{E} \cdot \mathbf{r}$$

is odd under the inversion operation (and hence can not be totally symmetric). This same analysis, when applied to $E_k^{(2)}$ shows that contributions to the second-order energy of an s orbital arise only from unperturbed orbitals ψ_j that are odd under inversion because only in such cases will the integrals $\langle s | e \mathbf{E} \cdot \mathbf{r} | \psi_j \rangle$ be non-zero.

II. The Møller-Plesset Perturbation Series

A. The Choice of H^0

Let us assume that an SCF calculation has been carried out using the set of N spin-orbitals $\{\psi_a\}$ that are occupied in the reference configuration ψ_k to define the corresponding Fock operator:

$$F = h + \sum_{a(\text{occupied})} [J_a - K_a] .$$

Further, we assume that all of the occupied $\{\psi_a\}$ and virtual $\{\psi_m\}$ spin-orbitals and orbital energies have been determined and are available.

This Fock operator is used to define the unperturbed Hamiltonian of Møller-Plesset perturbation theory (MPPT):

$$H^0 = \sum_i F(\mathbf{r}_i).$$

This particular Hamiltonian, when acting on any Slater determinant formed by placing N electrons into the SCF spin-orbitals, yields a zeroth order eigenvalue equal to the sum of the orbital energies of the spin-orbitals appearing in that determinant:

$$H^0 | \psi_{j_1 j_2 j_3 j_4 \dots j_N} \rangle = (\epsilon_{j_1} + \epsilon_{j_2} + \epsilon_{j_3} + \epsilon_{j_4} + \dots + \epsilon_{j_N}) | \psi_{j_1 j_2 j_3 j_4 \dots j_N} \rangle$$

because the spin-orbitals obey

$$F \psi_j = \epsilon_j \psi_j,$$

where j runs over all (occupied (a, b, ...) and virtual (m, n, ...)) spin-orbitals. This result is the MPPT embodiment of $H^0 \psi_k = E_k^0 \psi_k$.

B. The Perturbation V

The perturbation V appropriate to this MPPT case is the difference between the full N -electronic Hamiltonian and this H^0 :

$$V = H - H^0.$$

Matrix elements of V among determinantal wavefunctions constructed from the SCF spin-orbitals $\langle \psi_l | V | \psi_k \rangle$ can be expressed, using the Slater-Condon rules, in terms of matrix elements over the full Hamiltonian H

$$\langle \phi_k | V | \phi_k \rangle = \langle \phi_k | H | \phi_k \rangle - \sum_{i,j} E_k^0,$$

because each such determinant is an eigenfunction of H^0 .

C. The MPPT Energy Corrections

Given this particular choice of H^0 , it is possible to apply the general RSPT energy and wavefunction correction formulas developed above to generate explicit results in terms of spin-orbital energies and one- and two-electron integrals, $\langle \phi_i | h | \phi_j \rangle$ and $\langle \phi_i \phi_j | g | \phi_k \phi_l \rangle = \langle ij | kl \rangle$, over these spin-orbitals. In particular, the first-order energy correction is given as follows:

$$\begin{aligned} E_k^{(1)} &= \langle \phi_k | V | \phi_k \rangle = \langle \phi_k | H | \phi_k \rangle - \sum_a \epsilon_a \\ &= \sum_a \epsilon_a - \sum_{a,b} [J_{a,b} - K_{a,b}] - \sum_a \epsilon_a \\ &= - \sum_{a,b} [J_{a,b} - K_{a,b}] = - \sum_{a,b} [\langle ab | ab \rangle - \langle ab | ba \rangle]. \end{aligned}$$

Thus E_k^0 (the sum of orbital energies) and $E_k^{(1)}$ (the correction for double counting) add up to produce the proper expectation value energy.

The second-order energy correction can be evaluated in like fashion by noting that $\langle \phi_k | H | \phi_l \rangle = 0$ according to the Brillouin theorem for all singly excited ϕ_l , and that $\langle \phi_k | H | \phi_l \rangle = \langle ab | mn \rangle - \langle ab | nm \rangle$ for doubly excited ϕ_l in which excitations from ϕ_a and ϕ_b into ϕ_m and ϕ_n are involved:

$$\begin{aligned} E_k^{(2)} &= \sum_j \frac{|\langle \phi_j | V | \phi_k \rangle|^2}{E_k^0 - E_j^0} \\ &= \sum_{a,b;m<n} \frac{|\langle ab | mn \rangle - \langle ab | nm \rangle|^2}{\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n}. \end{aligned}$$

D. The Wavefunction Corrections

The first-order MPPT wavefunction can be evaluated in terms of Slater determinants that are excited relative to the SCF reference function ϕ_k . Realizing again that the perturbation coupling matrix elements $\langle \phi_k | H | \phi_l \rangle$ are non-zero only for doubly excited CSF's, and denoting such doubly excited ϕ_l by $\phi_{a,b;m,n}$, the first-order wavefunction can be written as:

$$\begin{aligned} \phi_k^{(1)} &= \sum_j \frac{\langle \phi_j | V | \phi_k \rangle}{E_k^0 - E_j^0} | \phi_j \rangle \\ &= \sum_{a,b;m<n} \phi_{a,b;m,n} [\langle ab | mn \rangle - \langle ab | nm \rangle] / (\epsilon_a + \epsilon_b - \epsilon_m - \epsilon_n). \end{aligned}$$

III. Conceptual Use of Perturbation Theory

The first- and second- order RSPT energy and first-order RSPT wavefunction correction expressions form not only a useful computational tool but are also of great use in understanding how strongly a perturbation will affect a particular state of the system. By

examining the symmetries of the state of interest ψ_k (this can be an orbital of an atom or molecule, an electronic state of same, or a vibrational/rotational wavefunction of a molecule) and of the perturbation V , one can say whether V will have a significant effect on the energy E_k of ψ_k ; if $\langle \psi_k | V | \psi_k \rangle$ is non-zero, the effect can be expected to be significant.

Sometimes the perturbation is of the wrong symmetry to directly (i.e., in a first-order manner) affect E_k . In such cases, one considers whether nearby states $\{ \psi_j, E_j \}$ exist which could couple through V with ψ_k ; the second-order energy expression, which contains $\sum_j |\langle \psi_j | V | \psi_k \rangle|^2 / [E_k^0 - E_j^0]$ directs one to seek states whose symmetries are contained in the direct product of the symmetries of V and of ψ_k and which are close to E_k in energy.

It is through such symmetry and 'coupling matrix element' considerations that one can often 'guess' whether a given perturbation will have an appreciable effect on the state of interest.

The nature of the perturbation is not important to such considerations. It could be the physical interaction that arises as two previously non-interacting atoms are brought together (in which case V would have axial point group symmetry) or it could describe the presence of surrounding ligands on a central transition metal ion (in which case V would carry the symmetry of the 'ligand field'). Alternatively, the perturbation might describe the electric dipole interaction of the electrons and nuclei of the atom or molecule with an externally applied electric field \mathbf{E} , in which case $V = - \sum_j e \mathbf{r}_j \cdot \mathbf{E} + \sum_a Z_a e \mathbf{R}_a \cdot \mathbf{E}$ contains components that transform as x , y , and z in the point group appropriate to the system (because the electronic \mathbf{r}_j and nuclear \mathbf{R}_a coordinate vectors so transform).