

Lecture 23, March 22, 2006

(Some material in this lecture has been adapted from Cramer, C. J. *Essentials of Computational Chemistry*, Wiley, Chichester: 2002; pp. 204-206, 460-463.)

Solved Homework

We need to evaluate $\langle H \rangle$ for the open-shell singlet. Thus

$$\begin{aligned}
 \langle 1s2\bar{s} | H | 1s2\bar{s} \rangle &= \left\langle \left[1s(1)2s(2) + 1s(2)2s(1) \right] \left[\alpha(1)\beta(2) - \alpha(2)\beta(1) \right] H \right\rangle \\
 &= \left\langle \left[1s(1)2s(2) + 1s(2)2s(1) \right] H \left[1s(1)2s(2) + 1s(2)2s(1) \right] \right\rangle \\
 &= \frac{1}{2} \left[\left\langle 1s(1) \left| -\frac{1}{2} \nabla_1^2 \right| 1s(1) \right\rangle + \left\langle 1s(1) \left| -\frac{2}{r_1} \right| 1s(1) \right\rangle \right. \\
 &\quad + \left\langle 1s(2) \left| -\frac{1}{2} \nabla_2^2 \right| 1s(2) \right\rangle + \left\langle 1s(2) \left| -\frac{2}{r_2} \right| 1s(2) \right\rangle \\
 &\quad + \left\langle 2s(1) \left| -\frac{1}{2} \nabla_1^2 \right| 2s(1) \right\rangle + \left\langle 2s(1) \left| -\frac{2}{r_1} \right| 2s(1) \right\rangle \\
 &\quad + \left\langle 2s(2) \left| -\frac{1}{2} \nabla_2^2 \right| 2s(2) \right\rangle + \left\langle 2s(2) \left| -\frac{2}{r_2} \right| 2s(2) \right\rangle \\
 &\quad + \left\langle 1s(1)2s(2) \left| \frac{1}{r_{12}} \right| 1s(1)2s(2) \right\rangle + \left\langle 1s(2)2s(1) \left| \frac{1}{r_{12}} \right| 1s(2)2s(1) \right\rangle \\
 &\quad \left. + \left\langle 1s(1)2s(2) \left| \frac{1}{r_{12}} \right| 1s(2)2s(1) \right\rangle + \left\langle 1s(2)2s(1) \left| \frac{1}{r_{12}} \right| 1s(1)2s(2) \right\rangle \right] \\
 &= \varepsilon_{1s} + \varepsilon_{2s} + J_{1s2s} + K_{1s2s}
 \end{aligned}$$

Step 1: insert the actual determinant with normalization implicit. Step 2: integrate over spin to arrive at a factor of one since the singlet spin function is normalized. Step 3: Expand the Hamiltonian into its one-electron and two-electron terms. Since each one-electron term allows integration over the other electron's coordinates (to give one or zero) these integrals are simplified. Note, however, that because of the nature of the *spatial* wave function there are 4 terms involving the $1/r_{12}$ operator, every one of which is positive. The change in sign for the exchange integrals K , resulting from the "+" in the

spatial wave function in contrast to the "-" in the spatial wave function of the $M_S = 0$ triplet, is what accounts for the change in sign of K in the final energy expression, and why the open-shell singlet is above the triplet in energy.

Perturbation Theory

Often in eigenvalue equations, the nature of a particular operator makes it difficult to work with. However, it is sometimes worthwhile to create a more tractable operator by removing some particularly unpleasant portion of the original one. Using exact eigenfunctions and eigenvalues of the simplified operator, it is possible to estimate the eigenfunctions and eigenvalues of the more complete operator. Rayleigh-Schrödinger perturbation theory provides a prescription for accomplishing this.

In the general case, we have some operator \mathbf{A} that we can write as

$$\mathbf{A} = \mathbf{A}^{(0)} + \lambda \mathbf{V} \quad (23-1)$$

where $\mathbf{A}^{(0)}$ is an operator for which we *can* find eigenfunctions, \mathbf{V} is a perturbing operator, and λ is a dimensionless parameter that, as it varies from 0 to 1, maps $\mathbf{A}^{(0)}$ into \mathbf{A} . If we expand our ground-state (indicated by a subscript 0) eigenfunctions and eigenvalues as Taylor series in λ , we have

$$\Psi_0 = \Psi_0^{(0)} + \lambda \left. \frac{\partial \Psi_0^{(0)}}{\partial \lambda} \right|_{\lambda=0} + \frac{1}{2!} \lambda^2 \left. \frac{\partial^2 \Psi_0^{(0)}}{\partial \lambda^2} \right|_{\lambda=0} + \frac{1}{3!} \lambda^3 \left. \frac{\partial^3 \Psi_0^{(0)}}{\partial \lambda^3} \right|_{\lambda=0} + \dots \quad (23-2)$$

and

$$a_0 = a_0^{(0)} + \lambda \left. \frac{\partial a_0^{(0)}}{\partial \lambda} \right|_{\lambda=0} + \frac{1}{2!} \lambda^2 \left. \frac{\partial^2 a_0^{(0)}}{\partial \lambda^2} \right|_{\lambda=0} + \frac{1}{3!} \lambda^3 \left. \frac{\partial^3 a_0^{(0)}}{\partial \lambda^3} \right|_{\lambda=0} + \dots \quad (23-3)$$

where $a_0^{(0)}$ is the eigenvalue for $\Psi_0^{(0)}$, which is the appropriate normalized ground-state eigenfunction for $\mathbf{A}^{(0)}$. For ease of notation, eqs. 23-2 and 23-3 are usually written as

$$\Psi_0 = \Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \dots \quad (23-4)$$

and

$$a_0 = a_0^{(0)} + \lambda a_0^{(1)} + \lambda^2 a_0^{(2)} + \lambda^3 a_0^{(3)} + \dots \quad (23-5)$$

where the terms having superscripts (n) are referred to as “ n th-order corrections” to the zeroth order term and are defined by comparison to eqs. 23-2 and 23-3.

Thus, we may write

$$\left(\mathbf{A}^{(0)} + \lambda \mathbf{V}\right) |\Psi_0\rangle = a_0 |\Psi_0\rangle \quad (23-6)$$

as

$$\begin{aligned} \left(\mathbf{A}^{(0)} + \lambda \mathbf{V}\right) \left|\Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \dots\right\rangle = \\ \left(a_0^{(0)} + \lambda a_0^{(1)} + \lambda^2 a_0^{(2)} + \lambda^3 a_0^{(3)} + \dots\right) \left|\Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \lambda^3 \Psi_0^{(3)} + \dots\right\rangle \end{aligned} \quad (23-7)$$

Since eq. 23-7 is valid for *any* choice of λ between 0 and 1, we can expand the left and right sides and consider only equalities involving like powers of λ . Powers 0 through 3 require

$$\mathbf{A}^{(0)} |\Psi_0^{(0)}\rangle = a_0^{(0)} |\Psi_0^{(0)}\rangle \quad (23-8)$$

$$\mathbf{A}^{(0)} |\Psi_0^{(1)}\rangle + \mathbf{V} |\Psi_0^{(0)}\rangle = a_0^{(0)} |\Psi_0^{(1)}\rangle + a_0^{(1)} |\Psi_0^{(0)}\rangle \quad (23-9)$$

$$\mathbf{A}^{(0)} |\Psi_0^{(2)}\rangle + \mathbf{V} |\Psi_0^{(1)}\rangle = a_0^{(0)} |\Psi_0^{(2)}\rangle + a_0^{(1)} |\Psi_0^{(1)}\rangle + a_0^{(2)} |\Psi_0^{(0)}\rangle \quad (23-10)$$

$$\mathbf{A}^{(0)} |\Psi_0^{(3)}\rangle + \mathbf{V} |\Psi_0^{(2)}\rangle = a_0^{(0)} |\Psi_0^{(3)}\rangle + a_0^{(1)} |\Psi_0^{(2)}\rangle + a_0^{(2)} |\Psi_0^{(1)}\rangle + a_0^{(3)} |\Psi_0^{(0)}\rangle \quad (23-11)$$

where further generalization should be obvious. Our goal, of course, is to determine the various n th-order corrections. Eq. 23-8 is the zeroth-order solution from which we are hoping to build, while eq. 23-9 involves the two unknown first-order corrections to the wave function and eigenvalue.

To proceed, we first impose intermediate normalization of Ψ_0 ; that is

$$\langle \Psi_0 | \Psi_0^{(0)} \rangle = 1 \quad (23-12)$$

By use of eq. 23-4 and normalization of $\Psi_0^{(0)}$, it must then be true that

$$\langle \Psi_0^{(n)} | \Psi_0^{(0)} \rangle = \delta_{n0} \quad (23-13)$$

Now, we multiply on the left by $\Psi_0^{(0)}$ and integrate to solve eqs. 23-9 to 23-11. In the case of eq. 23-9, we have

$$\langle \Psi_0^{(0)} | \mathbf{A}^{(0)} | \Psi_0^{(1)} \rangle + \langle \Psi_0^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle = a_0^{(0)} \langle \Psi_0^{(0)} | \Psi_0^{(1)} \rangle + a_0^{(1)} \langle \Psi_0^{(0)} | \Psi_0^{(0)} \rangle \quad (23-14)$$

Noting that the turnover rule implies

$$\begin{aligned}\langle \Psi_0^{(0)} | \mathbf{A}^{(0)} | \Psi_0^{(1)} \rangle &= \langle \mathbf{A}^{(0)} \Psi_0^{(0)} | \Psi_0^{(1)} \rangle \\ &= a_0^{(0)} \langle \Psi_0^{(0)} | \Psi_0^{(1)} \rangle \\ &= 0\end{aligned}\quad (23-15)$$

we can simplify eq. 23-15 to

$$\langle \Psi_0^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle = a_0^{(1)} \quad (23-16)$$

which is a well known result that *the first order correction to the eigenvalue is the expectation value of the perturbation operator over the unperturbed wave function.*

Note that we did 1st order perturbation theory without realizing it in lecture 18. We said that we realized that we could not solve the Schrödinger equation for He because of the $1/r_{12}$ term, so we decided to remove it. The resulting operator permitted exact solutions (since it was a separable combination of 2 one-electron operators) with the ground state being a product of one-electron 1s orbitals. We then evaluated the energy as the sum of the 1s orbital energies *plus* $\langle 1/r_{12} \rangle$ evaluated over the exact wave function for the simplified operator (i.e., exactly eq. 23-16)—that's first-order perturbation theory. It's really pretty easy.

As for $\Psi_0^{(1)}$, like *any* function of the electronic coordinates, it can be expressed as a linear combination of the complete set of eigenfunctions of $\mathbf{A}^{(0)}$, i.e.,

$$\Psi_0^{(1)} = \sum_j c_j \Psi_j^{(0)} \quad (23-17)$$

To determine the coefficients c_j in eq. 23-17, we can multiple eq. 23-9 on the left by $\Psi_j^{(0)}$ and integrate to obtain

$$\langle \Psi_j^{(0)} | \mathbf{A}^{(0)} | \Psi_0^{(1)} \rangle + \langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle = a_0^{(0)} \langle \Psi_j^{(0)} | \Psi_0^{(1)} \rangle + a_0^{(1)} \langle \Psi_j^{(0)} | \Psi_0^{(0)} \rangle \quad (23-18)$$

Using eq. 23-17, we expand this to

$$\begin{aligned}\langle \Psi_j^{(0)} | \mathbf{A}^{(0)} | \sum_j c_j \Psi_j^{(0)} \rangle + \langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle &= \\ a_0^{(0)} \langle \Psi_j^{(0)} | \sum_j c_j \Psi_j^{(0)} \rangle + a_0^{(1)} \langle \Psi_j^{(0)} | \Psi_0^{(0)} \rangle &\end{aligned}\quad (23-19)$$

which, from the orthonormality of the zeroth-order eigenfunctions, simplifies to

$$c_j a_j^{(0)} + \langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle = c_j a_0^{(0)} \quad (23-20)$$

or

$$c_j = \frac{\langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle}{a_0^{(0)} - a_j^{(0)}} \quad (23-21)$$

With the first-order eigenvalue and wave function corrections in hand, one can carry out analogous operations to determine the second-order corrections, then the third-order, etc. The algebra is tedious, and we simply note the results for the second- and third-order eigenvalue corrections, namely

$$a_0^{(2)} = \sum_{j>0} \frac{|\langle \Psi_j^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle|^2}{a_0^{(0)} - a_j^{(0)}} \quad (23-22)$$

and

$$a_0^{(3)} = \sum_{j>0, k>0} \frac{\langle \Psi_0^{(0)} | \mathbf{V} | \Psi_j^{(0)} \rangle [\langle \Psi_j^{(0)} | \mathbf{V} | \Psi_k^{(0)} \rangle - \delta_{jk} \langle \Psi_0^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle] \langle \Psi_k^{(0)} | \mathbf{V} | \Psi_0^{(0)} \rangle}{(a_0^{(0)} - a_j^{(0)})(a_0^{(0)} - a_k^{(0)})} \quad (23-23)$$

The homework for tomorrow will involve use of some of these equations for a specific problem. For now, however, we will return to an issue presented previously without proof having to do with spectroscopic selection rules.

The below material is optional and non-testable

Spectroscopic Transition Probabilities

In electronic spectroscopy, one wants to know not only the energy difference between distinct electronic states, but also the probability that a transition between them will take place under appropriate circumstances. Thus, in the recording of a classic ultraviolet/visible spectrum for a molecule, the wavelengths of absorptions indicate the energetics of the transition, while the intensities of the absorptions indicate their “allowedness”, or probability.

The simplest approach to understanding the radiation- (light-) induced transition between electronic states is to invoke time-dependent perturbation theory. Thus, one starts from the time-dependent Schrödinger equation

$$-\frac{\hbar}{i} \frac{\partial \Psi}{\partial t} = H\Psi \quad (23-24)$$

Recall that a complete set of eigenfunctions for eq. 23-24 is given by

$$\Psi_j = e^{-iE_j t / \hbar} \Phi_j \quad (23-25)$$

where the wave functions Φ_j are the eigenfunctions of the time-independent Schrödinger equation having eigenvalues E_j . Since the set of Ψ_j is complete, any wave function for the system may be expressed as

$$\Psi = \sum_k c_k e^{-iE_k t / \hbar} \Phi_k \quad (23-26)$$

where the normalized expansion coefficients c run over all possible eigenstates k .

We may consider the presence of a radiation field as a perturbation on the otherwise time-independent H^0 . Using the standard expression for the time-dependent electric field contribution to the Hamiltonian for radiation having a wavelength in the UV-visible light region we have

$$H = H^0 + e_0 \mathbf{r} \sin(2\pi\nu t) \quad (23-27)$$

where e_0 is the amplitude of the electric field associated with the light of frequency ν and \mathbf{r} is the usual position operator (the sum of the \mathbf{i} , \mathbf{j} , and \mathbf{k} operators in Cartesian space). With a time-dependent Hamiltonian, eq. 23-26 is still valid for the description of any wave function for the system, except that the expansion coefficients c must also be considered to be functions of t .

A spectroscopic measurement, from a quantum mechanical perspective, may thus be envisioned as the following process. The system begins in some stationary state, in which case all values of c in eq. 23-26 are 0, except for one, which is 1. For simplicity, we will consider the initial state to be the ground state, i.e., $c_0 = 1$. Beginning at time 0, the system is then exposed to radiation until time τ . During that time, the expansion coefficients will be in a constant state of change until, with the disappearance of the radiation, the Hamiltonian returns to being time independent, at which point the expansion coefficients for Ψ cease to change. To the extent more than one coefficient is non-zero, the system exists in a superposition of states and the probability of any particular state k being observed by experiment, determined from evaluation of $\langle \Psi | \Psi \rangle$, is simply c_k^2 .

To determine the latter probabilities, let us evaluate eq. 23-24 for an arbitrary wave function expressed in the form of eq. 23-26

$$-\frac{\hbar}{i} \frac{\partial}{\partial t} \sum_k c_k(t) e^{-iE_k t/\hbar} \Phi_k = \left[H^0 + e_0 \mathbf{r} \sin(2\pi\nu t) \right] \sum_k c_k(t) e^{-iE_k t/\hbar} \Phi_k \quad (23-28)$$

which may be expanded on both sides by explicitly taking the time derivative on the left and evaluating H^0 for the eigenfunctions on the right to

$$\begin{aligned} -\frac{\hbar}{i} \sum_k \frac{\partial c_k(t)}{\partial t} e^{-iE_k t/\hbar} \Phi_k + \sum_k c_k(t) E_k e^{-iE_k t/\hbar} \Phi_k \\ = \sum_k c_k(t) E_k e^{-iE_k t/\hbar} \Phi_k + e_0 \mathbf{r} \sin(2\pi\nu t) \sum_k c_k(t) e^{-iE_k t/\hbar} \Phi_k \end{aligned} \quad (23-29)$$

If we cancel the equivalent sums on the left and right we are left with

$$-\frac{\hbar}{i} \sum_k \frac{\partial c_k(t)}{\partial t} e^{-iE_k t/\hbar} \Phi_k = e_0 \mathbf{r} \sin(2\pi\nu t) \sum_k c_k(t) e^{-iE_k t/\hbar} \Phi_k \quad (23-30)$$

We now multiply on the left by Φ_m and integrate, where m indexes the stationary state Φ for which we are interested in measuring the probability of transition. This gives

$$-\frac{\hbar}{i} \sum_k \frac{\partial c_k(t)}{\partial t} e^{-iE_k t/\hbar} \langle \Phi_m | \Phi_k \rangle = e_0 \sin(2\pi\nu t) \sum_k c_k(t) e^{-iE_k t/\hbar} \langle \Phi_m | \mathbf{r} | \Phi_k \rangle \quad (23-31)$$

Note that the overlap integral on the l.h.s. of eq. 23-31 is simply δ_{mk} , because of the orthogonality of the stationary-state eigenfunctions. Thus, only the term $k = m$ survives, and we may rearrange the equation to

$$\frac{\partial c_m(t)}{\partial t} = -\frac{i}{\hbar} e_0 \sin(2\pi\nu t) \sum_k c_k(t) e^{-[i(E_m - E_k)t/\hbar]} \langle \Phi_m | \mathbf{r} | \Phi_k \rangle \quad (23-32)$$

If we *assume* that our perturbation was small, and applied for only a short time, we may further assume that the expansion coefficients on the r.h.s. of eq. 23-32 have their *initial* (ground-state) values (i.e., all equal to zero except for $c_0 = 1$). This leads to the further simplification

$$\frac{\partial c_m(t)}{\partial t} = -\frac{i}{\hbar} e_0 \sin(2\pi\nu t) e^{-[i(E_m - E_0)t/\hbar]} \langle \Phi_m | \mathbf{r} | \Phi_0 \rangle \quad (23-33)$$

In order to determine c_m at (and after) time τ , we must integrate t from 0 to τ , giving

$$\begin{aligned}
c_m(\tau) &= -\frac{i}{\hbar} e_0 \int_0^\tau \sin(2\pi\nu t) e^{-[i(E_m - E_0)t/\hbar]} \langle \Phi_m | \mathbf{r} | \Phi_0 \rangle dt \\
&= \frac{1}{2i\hbar} e_0 \left[\frac{e^{i(\omega_{m0} + \omega)\tau} - 1}{\omega_{m0} + \omega} - \frac{e^{i(\omega_{m0} - \omega)\tau} - 1}{\omega_{m0} - \omega} \right] \langle \Phi_m | \mathbf{r} | \Phi_0 \rangle
\end{aligned} \tag{23-34}$$

where

$$\omega = 2\pi\nu \tag{23-35}$$

and

$$\omega_{m0} = \frac{E_m - E_0}{\hbar} \tag{23-36}$$

What's it all mean? Well, let's now ask the *qualitative* question, for what values of m is $|c_m|^2$ large? Given a particular frequency of radiation ω , the magnitude of c_m will be large if ω_{m0} is close to ω , thereby making the denominator in the second term in brackets very small (note that even when ω_{m0} is equal to ω , the expansion coefficient is well behaved because of the way the numerator approaches zero, as a power series expansion of the exponential would show). This result is consistent with the notion that a photon of energy $h\nu$ is absorbed in the transition between the two states, although it takes a more sophisticated theoretical treatment to demonstrate this. However, this term fails to differentiate any one state m from another, all states being predicted to undergo transitions with equal probability at their respective frequencies.

It is the last term that accounts for differences in absorption probabilities. This term is the expectation value of the dipole moment operator (in a.u.) evaluated over different wave functions. Its expectation value is referred to as the transition dipole moment. As we discussed originally for the particle in a box, if $\langle \mu_{mn} \rangle = 0$, a transition is forbidden. Here, we have finally proven it.

End of optional material

Homework

To be solved in class:

Consider the particle of mass $m = 1$ in a box of length $L = 1$ with a bottom that is not perfectly horizontal. In particular, rather than the inside of the box having $V = 0$, it has a bottom sloping down to the right described by $V = k (1 - x)$ (i.e., linear, with height k at the left end and 0 at the right end). Calculate the ground-state energy of a particle in this box to first order in perturbation theory (fairly simple). Next, compute the ground state wave function to first order in perturbation theory and sketch its appearance (much more challenging). Explain the change in this wave function in an intuitive fashion.

To be turned in for possible grading Mar. 24:

Given eqs. 23-4 and 23-12, prove eq. 23-13.