Problem Set 6: Time-dependent properties & excited states.

Due in class, Tuesday April 1, 2008

1. Time-dependent perturbation theory refresher. If \( a_0(t = 0) = 1 \), then for a weak perturbation, \( \hat{H}^{(1)}(t) \), the first order perturbed wavefunction is:

\[
\Psi^{(1)}_0 = \sum_{j \neq 0} a_j(t) \Psi_j^{(0)} \exp[-iE_j^{(0)}t / \hbar]
\]

(a) Show that the expansion coefficients can be written as:

\[
a_j(t) \approx \frac{1}{i\hbar} \int_0^t dt' \langle \Psi_j^{(0)} | \hat{H}^{(1)}(t') | \Psi_j^{(0)} \rangle \exp[i\omega_j \omega' t']
\]

(b) Find the explicit form for these expansion coefficients when the time-dependent perturbation is

\[
\hat{H}^{(1)}(t) = \frac{1}{2} \mathbf{E} \cdot \mathbf{\mu} [e^{i\omega t} + e^{-i\omega t}]
\]

2. Schatz and Ratner q.5 p.109

3. Schatz and Ratner q.4 p.109 (please omit part (c)).

4. Time-dependent configuration interaction with singles (TD-CIS). For fixed orbitals satisfying the time-independent Hartree-Fock problem, consider a time-dependent perturbed wavefunction:

\[
\Psi_{\text{CIS}} = [c_0(t) \Phi_{\text{HF}}] + \sum_{ia} c_i^a(t) \Phi_i^a \exp[-iE_0t / \hbar]
\]

(a) Write out the equation of motion that the first order correction to the ground state HF wavefunction takes in the presence of a time-dependent perturbation. It can be written in the form:

\[
i\hbar \dot{\mathbf{a}} = (\mathbf{H} - E_0) \mathbf{a}
\]

(b) Derive the expression for the frequency-dependent polarizability in this model, giving spin-orbital expressions for the matrix elements.

(c) From the FDP, or the first order perturbed wavefunction, obtain an eigenvalue equation for the Bohr frequencies in this model. You should be able to show that it is the same as the Bohr frequencies associated with the CIS excited state model treated in lecture.

5. Model excited state calculations. Return to your favorite source (or web-site) of quantum chemistry programs and calculate the lowest vertical excitation energy of the formaldehyde molecule (CH2O) at its ground state equilibrium geometry (you may take standard bond lengths and angles if you wish, or optimize the geometry), using CIS, TDHF and TDDFT (with the B3LYP functional), and a reasonable basis set such as 6-31G*. Compare against the experimental value of approximately 4.0 eV.