Dec. 3, 2007

Chem. 1410
Problem Set 11

Do the following problems; these are *not* to be handed in for grading; solutions will be distributed via .pdf.

Engel: Q15.2, Q15.3, Q15.6, Q15.11

plus:

1) **Number of Unpaired Electrons in a Molecule**. Predict the number of unpaired electrons in i) NO and ii) CO.

2) **Franck-Condon Factor for Linearly Displaced Harmonic Oscillators.** Consider the situation shown schematically in Fig. 1, namely, potential energy functions corresponding to two electronic states of a diatomic molecule characterized by reduced mass μ. The internuclear separation is denoted here as *x*, while the ground state potential energy function is denoted as $V_g(x)$ and the excited state potential energy function as $V_e(x)$. Specifically, take:

$$V_g(x) = \frac{1}{2}kx^2 \quad ,$$

$$V_e(x) = \frac{1}{2}k(x-a)^2 + V_0 \quad .$$

Thus, the ground state potential energy function corresponds to a harmonic oscillator characterized by force constant *k* and centered at equilibrium position $x = 0$. The excited state potential energy function corresponds to a harmonic oscillator characterized by the *same* force constant, but with equilibrium position $x = a$ and energy origin V_0 (compared with energy origin 0 for the ground state potential function).

a) What frequency of light is absorbed to induce a transition from the ground vibrational state of the ground potential function to the ground vibrational state of the excited state potential function?

b) The intensity of this transition I is given to within a constant of proportionality by:

$$I = \left| \int_{-\infty}^{\infty} dx \phi_0^{(g)}(x) \phi_0^{(e)}(x) \right|^2$$

where $\phi_0^{(g)}(x)$ is the (normalized) vibrational ground state eigenfunction of the ground electronic state, and $\phi_0^{(e)}(x)$ is the corresponding vibrational ground state eigenfunction of the excited electronic state. Calculate *I*.

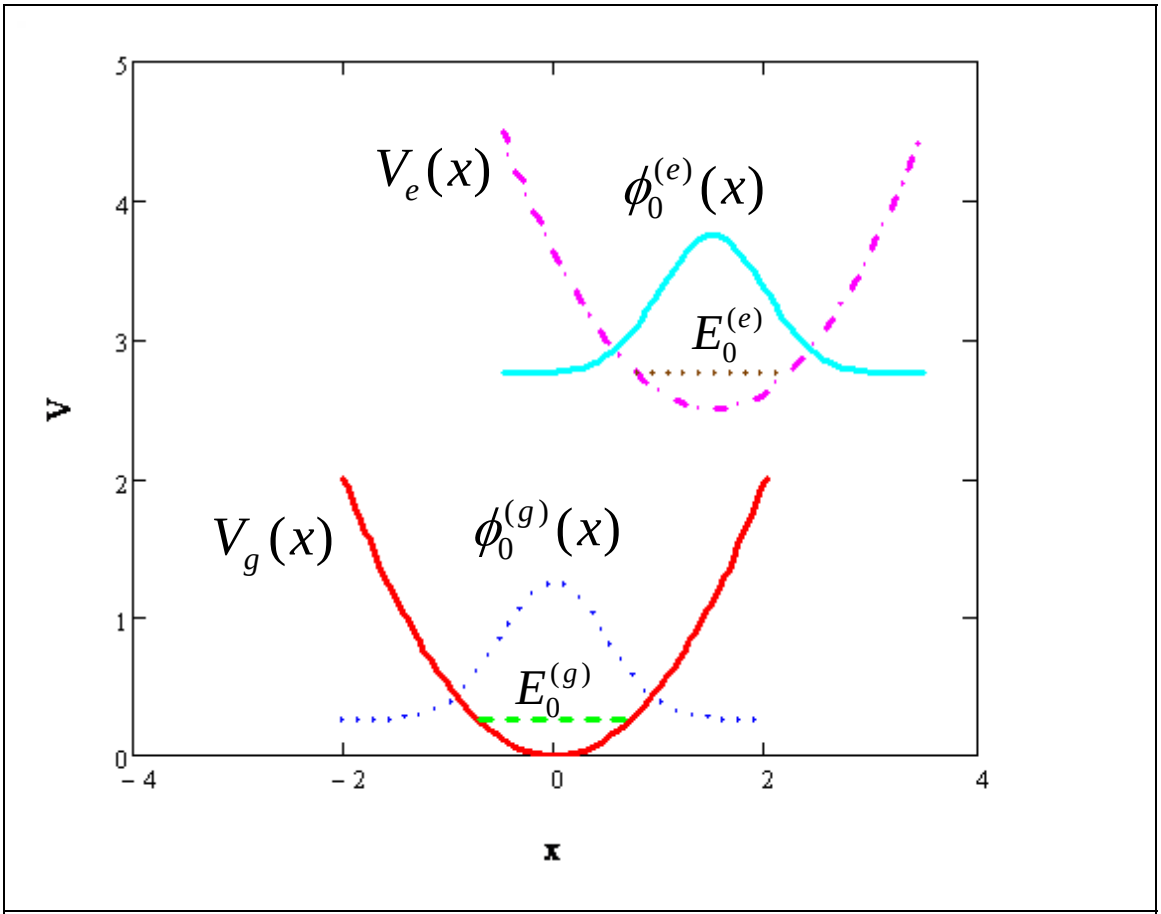

Fig. 1 Two harmonic oscillator potential energy functions, displaced horizontally and vertically from each other: the horizontal displacement is *a*; the vertical displacement is V_0. The ground state energy level and eigenfunction are indicated schematically for both ground and excited electronic potential energy functions. [Note: Ignore the tick mark numbers on the *x* and *V* axes. These are for illustrative purposes only.]