CHEM 6472: Quantum Mechanics

Problem Set V

Due Thursday, Oct. 24

1. Consider a 2-D harmonic oscillator with potential $V(x, y) = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2$. What are the eigenvalues and eigenfunctions?

2. **The Harmonic Oscillator as a model of molecular vibrations in diatomic molecules.**

   Consider a diatomic molecule AB. The total wavefunction for this molecule may be approximately factorized as

$$\Psi(\mathbf{r}, \mathbf{R}) = \Psi_{trans}(\mathbf{R}_{CM})\Psi_{vib}(R)\Psi_{rot}(\theta, \phi; R)\Psi_{elec}(\mathbf{r}; \mathbf{R}), \tag{1}$$

   where $\mathbf{R}$ and $\mathbf{r}$ denote nuclear and electronic degrees of freedom, respectively, $\mathbf{R}_{CM}$ denotes the center of mass coordinates, R is the distance between nuclei, and θ, ϕ denote rotations of the diatomic about some fixed coordinate system. A coordinate after a semicolon means that the wavefunction depends on that variable *parametrically* — i.e., we pretend the wavefunction does not depend on that variable, but we solve for the wavefunction at a series of different values for the parametric variable and obtain different results each time.

   Using the simple relationship $S_{vib}(R) = \Psi_{vib}(R)/R$, it is possible, after invoking the Born-Oppenheimer approximation and some other approximations, to arrive at the "vibrational Schrödinger equation":

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2 S_{vib}(q)}{dq^2} + E_{elec}(q)S_{vib}(q)\right] = E_{vib}S_{vib}(q), \tag{2}$$

   where we have switched over to a new variable q which is just the deviation of the bond length R from its equilibrium value R_e, or $q = R - R_e$. Note also that we have turned the two-body vibrational problem into a one-body problem by switching to center-of-mass coordinates and invoking the reduced mass

$$\mu = \frac{M_A M_B}{M_A + M_B}. \tag{3}$$

   (a) Suppose we have the molecule HCl. Assuming the most common isotopes of H and Cl atoms, what is the reduced mass of this molecule? Note: you need the actual mass of a single H atom and a single Cl atom, not a mole of them; do not use masses from a periodic table, since these average over naturally occuring isotopic abundances. One quantum of energy for HCl can be obtained spectroscopically as 2991 cm^{-1}. (This is an unusual energy unit ("wavenumbers") which can be converted to a real unit of energy by multiplying by hc or to angular frequency ω by multiplying by $2\pi c$). What is the force constant for the H–Cl bond in units of kg s^{-2}?

(b) Expand $E_{elec}(q)$ as a Taylor series about $q = 0$ (i.e., about the equilibrium bond length $R = R_e$), to obtain

$$E_{elec}(q) = E_{elec}(0) + E'_{elec}(0)q + \frac{1}{2}E''_{elec}(0)q^2 + \cdots \tag{4}$$

Now assume that the cubic and higher terms are all negligible. This is called the assumption of *mechanical harmonicity.* Eq. (4), when cubic and higher terms are neglected, leads to an equation which is equivalent to the Harmonic Oscillator problem when fed into eq. (2). At $R = R_e$ (or $q = 0$), we are at a minimum on the potential energy curve, so $E'_{elec}(0) = 0$. Explain why the constant term $E_{elec}(0)$ (which does not appear in the Harmonic Oscillator problem) does not really make this a different problem than the Harmonic Oscillator, and identify the oscillator force constant in terms of the factors appearing in eq. (4).

(c) *Infrared Spectra:* A photon of light can be absorbed or emitted by our diatomic molecule if it has exactly the same energy as an allowed transition between energy levels in the molecule *and* if the transition between these levels is "allowed." A transition between levels is allowed if there is some mechanism coupling the two levels. Most frequently, we are concerned with "electric dipole allowed" transitions, which means that we obtain a nonzero value for the "transition matrix element" between two states $|\Psi'\rangle$ and $|\Psi\rangle$:

$$\langle\Psi'|\mu|\Psi\rangle = \Psi'_{trans}(\mathbf{R}_{CM})\Psi'_{elec}(\mathbf{r})\Psi'_{vib}(R)\Psi'_{rot}(\theta,\phi)\mu\Psi_{trans}(\mathbf{R}_{CM})\Psi_{elec}(\mathbf{r})\Psi_{vib}(R)\Psi_{rot}(\theta,\phi). \tag{5}$$

Note that μ is a vector, $\mu = \mu_x\hat{i} + \mu_y\hat{j} + \mu_z\hat{k}$. Since we can express μ in terms of purely internal coordinates, the translational part factors out and integrates to a factor of one if we are in the same translational state. Furthermore, let us assume we are in the same electronic and rotational states for $|\Psi\rangle$ and $|\Psi'\rangle$ just to make things easier. Then,

$$\langle\Psi'|\mu|\Psi\rangle = \int dRR^2\frac{S'^*_{vib}}{R}\int d\Omega\Psi^*_{rot}(\theta,\phi;R)\int d\mathbf{r}\Psi^*_{elec}(\mathbf{r};\mathbf{R})\mu\frac{S_{vib}}{R}\Psi_{rot}(\theta,\phi;R)\Psi_{elec}(\mathbf{r};\mathbf{R}). \tag{6}$$

If we lump together everything but the vibrational part into a new variable (vector),

$$\mathbf{d}(R) = \int d\Omega\Psi^*_{rot}(\theta,\phi;R)\int d\mathbf{r}\Psi^*_{elec}(\mathbf{r};\mathbf{R})\mu\Psi_{rot}(\theta,\phi;R)\Psi_{elec}(\mathbf{r};\mathbf{R}), \tag{7}$$

then we finally get a simple expression for the intensity of a transition between different vibrational levels (which will appear in the infrared):

$$\langle\Psi'|\mu|\Psi\rangle = \int dRS'^*_{vib}(R)\mathbf{d}(R)S_{vib}(R), \tag{8}$$

which can be rewritten in terms of our displacement variable q:

$$\langle\Psi'|\mu|\Psi\rangle = \int dqS'^*_{vib}(q)\mathbf{d}(q)S_{vib}(q). \tag{9}$$

Since the $S_{vib}(q)$ wavefunctions are just our Harmonic oscillator wavefunctions, and since these are conveniently indexed by a single quantum number n, we'll rewrite the vibrational wavefunctions in $|\Psi'\rangle$ and $|\Psi\rangle$ as $|n\rangle$ and $|m\rangle$, respectively, to obtain:

$$\langle\Psi'|\mu|\Psi\rangle = \int \langle n|\mathbf{d}(q)|m\rangle dq. \tag{10}$$

i. Expand $\mathbf{d}(q)$ in a Taylor series in q about $q = 0$. As it turns out, this expansion is very strongly dominated by just the first two or three terms. If you keep only the constant term, what combinations of quantum numbers n and m, if any, give allowed transition matrix elements in eq. (10)?

ii. The linear term is usually the one which determines spectra. What combinations of quantum numbers n and m give nonzero transitions for the term of $\mathbf{d}(q)$ linear in q? This is in fact the famous "selection rule" for IR transitions!

iii. Finally, sometimes weak transitions can be observed due to the quadratic (or higher) terms in the expansion of $\mathbf{d}(q)$. What is the selection rule for the term quadratic in q?