5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #2 Supplement

Contents

A Matrix Solution of Harmonic Oscillator Problem

We wish to obtain all possible information about the eigenstates of a harmonic oscillator without ever solving for the actual eigenfunctions. The energy levels and the expectation values of any positive integer power of $\mathbf{x}= r - r_e$ and $\mathbf{p} = m\frac{dx}{dt}$ will be obtained.

The first step is always to write down the Hamiltonian operator, which for the harmonic oscillator is:

$$\mathbf{H} = \frac{p^2}{2m} + \frac{kx^2}{2} \tag{1}$$

In order to construct the matrix for $\mathbf{H}$ we need to know the matrix elements of $\mathbf{p}^2$ and $\mathbf{x}^2$ in some convenient basis set. Because we are lazy (and clever) we would like to choose a basis set which results in a diagonal $\mathbf{H}$ matrix. We know such a basis set must exist (because any Hermitian matrix can be diagonalized), so we choose that basis set and try to obtain the $\mathbf{p}$ and $\mathbf{x}$ matrices in that basis without initially knowing the properties of those basis functions. We know:

A. $\mathbf{H}$ is in diagonal form (choice of basis);

B. $[\mathbf{x}, \mathbf{p}] = \mathbf{xp} - \mathbf{px} = i\hbar$ (a fundamental postulate of quantum mechanics;

C. $\frac{d}{dt}\mathbf{A} = \frac{1}{i\hbar}[\mathbf{A}, \mathbf{H}] + \frac{\partial \mathbf{A}}{\partial t}$ for any operator $\mathbf{A}$ (the Heisenberg equation of motion, derived in the appendix of this handout).

$$\begin{aligned} &\mathbf{p} = m\dot{\mathbf{x}} \\ &p_{ik} = \frac{m}{i\hbar}[\mathbf{x}, \mathbf{H}]_{ik} = \frac{m}{i\hbar}\left[\sum_j (x_{ij}H_{jk} - H_{ij}x_{jk})\right] \end{aligned} \tag{2}$$

The force is

$$\mathbf{F} = \dot{\mathbf{p}} = \frac{1}{i\hbar}[\mathbf{p}, \mathbf{H}] \tag{3}$$

but also

$$\mathbf{F} = -\nabla \mathbf{V} = -\frac{d}{dx}\left(\frac{kx^2}{2}\right) = -k\mathbf{x} \tag{4}$$

so

$$\mathbf{x} = -\left(\frac{1}{k}\right)\frac{1}{i\hbar}[\mathbf{p}, \mathbf{H}] \tag{5}$$

$$x_{ik} = \frac{i}{\hbar k}\left[\sum_j (p_{ij}H_{jk} - H_{ij}p_{jk})\right] \tag{6}$$

Equations (2) and (6) are coupled operator equations. We uncouple them by using the diagonal property of $\mathbf{H}$.
From Eq. (2)

$$p_{ik} = \frac{m}{i\hbar}x_{ik}(H_{kk} - H_{ii}) \tag{7}$$

$$x_{ik} = \frac{i}{\hbar k}p_{ik}(H_{kk} - H_{ii}) \tag{8}$$

now multiply (7) by x_{ik} and (8) by p_{ik} and equating

$$\frac{m}{i\hbar}(x_{ik})^2(H_{kk} - H_{ii}) = \frac{i}{\hbar k}(p_{ik})^2(H_{kk} - H_{ii}) \tag{9}$$

if $i \neq k$, then (otherwise we would be dividing by zero)

$$x_{ik}^2 = -\frac{1}{km}p_{ik}^2 \tag{10}$$

Thus

$$\boxed{x_{ik} = \pm\frac{i}{\sqrt{km}}p_{ik}} \tag{11}$$

Return to equations (7) and (8) and note that if $i = k$, then both p_{ii} and x_{ii} are zero. This means that neither the $\mathbf{p}$ nor the $\mathbf{x}$ matrices have any diagonal matrix elements.
If we now plug (11) into equation (7) we get

$$p_{ik} = \frac{m}{i\hbar}\left(\pm\frac{i}{\sqrt{km}}\right)p_{ik}(H_{kk} - H_{ii}). \tag{12}$$

If and only if $p_{ik} \neq 0$, we can divide through by p_{ik} and rearrange

$$\boxed{H_{kk} - H_{ii} = \pm\hbar\sqrt{\frac{k}{m}} = h\nu} \tag{13}$$

If $H_{kk} - H_{ii} \neq \pm h\nu$, then $p_{ik} = 0$ (and also $x_{ik} = 0$). This means that the energy levels of the harmonic oscillator are evenly spaced and separated by $h\nu$. So

$$H_{ii} = \hbar\sqrt{\frac{k}{m}}(n + \alpha)$$

where n is an integer and α is undetermined. Note the requirement that if $H_{kk} - H_{ii} \neq \pm h\nu$, $p_{ik} = x_{ik} = 0$ implies that the only non-zero p_{ik} and x_{ik} are those where $k = i \pm 1$. Actually it is necessary to assume that the eigenvalues of $\mathbf{H}$ are non-degenerate and increase monotonically with index. Now use $[\mathbf{x}, \mathbf{p}] = i\hbar$ to get matrix elements of $\mathbf{x}$ and $\mathbf{p}$.

$$\sum_j (x_{ij}p_{jk} - p_{ij}x_{jk}) = i\hbar\delta_{ik}. \tag{14}$$

The δ_{ik} (delta function) comes from the orthogonality of our basis set. The sum in equation (14) consists of only two terms corresponding to the only non-zero **p** and **x** matrix elements.

$$(x_{i,i+1}p_{i+1,i} - p_{i,i+1}x_{i+1,i}) + (x_{i,i-1}p_{i-1,i} - p_{i,i-1}x_{i-1,i}) = i\hbar. \tag{15}$$

Since there is a lowest energy that corresponds to the lowest value of the index, when $i = 1$

$$p_{i,i-1} = x_{i,i-1} = 0$$

is required because no eigenstates exist with $i < 1$. Thus

$$x_{12}p_{21} - p_{12}x_{21} = i\hbar. \tag{16}$$

Employing the Hermitian property of **p** and **x**.

$$x_{12}p_{12}^* - p_{12}x_{12}^* = i\hbar \tag{17}$$

inserting equation (11)

$$x_{12}x_{12}^*\left(\pm\frac{\sqrt{km}}{i}\right) - x_{12}x_{12}^*\left(\pm\frac{\sqrt{km}}{i}\right) = i\hbar. \tag{18}$$

$$\text{Thus} \qquad x_{12}x_{12}^* = i\hbar\left(\mp\frac{i}{i2\sqrt{km}}\right) \tag{19}$$

$$\boxed{\begin{aligned} |x_{12}|^2 &= \frac{\hbar}{2\sqrt{km}} \qquad (20) \\ |p_{12}|^2 &= km|x_{12}|^2 = \frac{\sqrt{km}}{2}\hbar \qquad (21) \end{aligned}}$$

Now go back to equation (15) and consider the general case

$$\frac{\sqrt{km}}{i}\left[-|x_{n,n+1}|^2 - |x_{n,n+1}|^2 - |x_{n,n-1}|^2 - |x_{n,n-1}|^2\right] = i\hbar$$

Thus

$$|x_{n,n+1}|^2 = |x_{n,n-1}|^2 + \frac{\hbar}{2\sqrt{km}}. \tag{22}$$

Now, if we re-index, letting $n = 0$ correspond to the lowest eigenstate,

$$\begin{aligned} |x_{n,n+1}|^2 &= \frac{(n+1)\hbar}{2\sqrt{km}} \\ |p_{n,n+1}|^2 &= \frac{(n+1)\hbar\sqrt{km}}{2} \end{aligned} \tag{23}$$

and in order to get values for $x_{n,n\pm1}$ and $p_{n,n\pm1}$ we have to choose phase consistent with equation (11):

$$\begin{aligned} x_{n,n+1} &= \sqrt{\frac{(n+1)\hbar}{2\sqrt{km}}} \\ x_{n,n-1} &= \sqrt{\frac{n\hbar}{2\sqrt{km}}} \\ p_{n,n+1} &= -i\sqrt{\frac{(n+1)\hbar\sqrt{km}}{2}} \\ p_{n,n-1} &= i\sqrt{\frac{n\hbar\sqrt{km}}{2}}. \end{aligned} \tag{24}$$

Now evaluate H_{nn}.

$$\mathbf{H} = \frac{\mathbf{p}^2}{2m} + \frac{k\mathbf{x}^2}{2}$$

$$(\mathbf{p}^2)_{nn} = \sum_m \langle n|\mathbf{p}|m\rangle \langle m|\mathbf{p}|n\rangle = \langle n|\mathbf{p}|n+1\rangle \langle n+1|\mathbf{p}|n\rangle + \langle n|\mathbf{p}|n-1\rangle \langle n-1|\mathbf{p}|n\rangle = \frac{(2n+1)\hbar\sqrt{km}}{2}. \tag{25}$$

Similarly

$$(\mathbf{x})^2_{nn} = \frac{\hbar(2n+1)}{2\sqrt{km}}$$

$$\text{Thus} \qquad H_{nn} = \hbar\sqrt{\frac{k}{m}}\left(\frac{2n+1}{4} + \frac{2n+1}{4}\right) = \hbar\sqrt{\frac{k}{m}}\left(v + \frac{1}{2}\right). \tag{26}$$

Convince yourself now that $\mathbf{H}$ is diagonal.

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APPENDIX

B Derivation of Heisenberg Equation of Motion

The time dependent Schrödinger equation is

$$i\hbar\frac{\partial\psi}{\partial t} = \mathbf{H}\psi \tag{1}$$

We wish to know the time derivative of the matrix element of any operator $\mathbf{A}$ which corresponds to an observable quantity. This derivation will consider only the time derivative of the expectation value $\langle\mathbf{A}\rangle$ but can be generalized to include any matrix element of $\mathbf{A}$ by adding a prime to ψ^* wherever it appears below.

$$\frac{d}{dt}\langle\mathbf{A}\rangle = \frac{d}{dt}\int \psi^*\mathbf{A}\psi d\tau \tag{2}$$

Differentiate under integral and apply the chain rule $\left(\text{denote } \frac{d}{dt} \text{ by}^{\cdot}\right)$

$$\frac{d}{dt}\langle\mathbf{A}\rangle = \int\left(\dot{\psi}^*\mathbf{A}\psi + \psi^*\dot{\mathbf{A}}\psi + \psi^*\mathbf{A}\dot{\psi}\right)d\tau \tag{3}$$

Evaluate the first and third terms by inserting $\dot{\psi} = \frac{1}{i\hbar}\mathbf{H}\psi$ or the complex conjugate from equation (1).

$$\frac{d}{dt}\langle\mathbf{A}\rangle = \int\left(-\frac{1}{i\hbar}\mathbf{H}\psi^*\mathbf{A}\psi + \psi^*\dot{\mathbf{A}}\psi + \frac{1}{i\hbar}\psi^*\mathbf{A}\mathbf{H}\psi\right)d\tau \tag{4}$$

$$= \frac{1}{i\hbar}\int\left(\psi^*\mathbf{A}\mathbf{H}\psi - \psi^*\mathbf{H}\mathbf{A}\psi + i\hbar\psi^*\dot{\mathbf{A}}\psi\right)d\tau \tag{5}$$

rearranging

$$i\hbar\frac{d}{dt}\langle\mathbf{A}\rangle = \int\left(\psi^*[\mathbf{A},\mathbf{H}]\psi + i\hbar\psi^*\dot{\mathbf{A}}\psi\right)d\tau$$

$$\text{or} \qquad i\hbar\dot{\mathbf{A}} = [\mathbf{A},\mathbf{H}] + i\hbar\frac{\partial\mathbf{A}}{\partial t} \tag{6}$$

where (6) is understood to be a matrix equation.

C Matrix Elements of any Function of X and P

For any vibrational problem, a harmonic oscillator basis set may be chosen. How are matrix elements of any function of X or P obtained?

Let $\mathbf{T}$ define the transformation which diagonalizes $\mathbf{H}$:

$$(\mathbf{T}^\dagger \mathbf{H} \mathbf{T}) = E_i \delta_{ij}. \tag{7}$$

$\mathbf{T}$ takes us to the energy basis. Let $\mathbf{S}$ define a different transformation which diagonalizes $\mathbf{X}$.

$$(\mathbf{S}^\dagger \mathbf{X} \mathbf{S})_{ij} = X_i \delta_{ij}. \tag{8}$$

$\mathbf{S}$ takes us from the harmonic basis to a (strange) position basis. It can be shown that an operator corresponding to any rational power of $\mathbf{X}$ (or a power series in $\mathbf{X}$) can be expressed as

$$\mathbf{X}^{a/b} = \mathbf{S}(\mathbf{S}^\dagger \mathbf{X} \mathbf{S})^{a/b} \mathbf{S}^\dagger = \mathbf{S}(X_i \delta_{ij})^{a/b} \mathbf{S}^\dagger \tag{9}$$

where the meaning of a diagonal matrix to a rational power is obvious. This result could be proved by noting that any power of a diagonal matrix is still diagonal and that $\mathbf{S}\mathbf{S}^\dagger = \mathbb{1}$ (unit matrix). The $\mathbf{X}^{a/b}$ matrix must finally be transformed to the energy basis:

$$\text{Observable } \mathbf{X}^{a/b} \text{ matrix} = \mathbf{T}^\dagger \mathbf{S}(\mathbf{S}^\dagger \mathbf{X} \mathbf{S})^{a/b} \mathbf{S}^\dagger \mathbf{T} \tag{10}$$