MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.61 Physical Chemistry
Fall, 2017

Professor Robert W. Field

FIFTY MINUTE EXAMINATION II ANSWERS

Thursday, October 26 @ 7:30 PM in 4-370

I. $\mathbf{a}^\dagger$ and a Matrices **(20 POINTS)**

A. (3 points) $\langle v+1|\mathbf{a}^\dagger|v\rangle = (v+1)^{1/2}$. Sketch the structure of the $\mathbf{a}^\dagger$ matrix below:

$$\mathbf{a}^\dagger = \begin{pmatrix} 0 & & & & & & \\ & 1 & & & & & \\ & & 2^{1/2} & & & & \\ & & & 3^{1/2} & & & \\ & & & & 4^{1/2} & & \\ & & & & & 5^{1/2} & \\ & & & & & & 6^{1/2} \\ & & & & & & & 0 \end{pmatrix}$$

B. (3 points) Now sketch the **a** matrix on a similar diagram.

$$\mathbf{a} = \begin{pmatrix} 0 & 1 & & & \\ & & 2^{1/2} & & \\ & & & 3^{1/2} & \\ & & & & 0 \end{pmatrix}$$

C. (5 points) Now apply $\mathbf{a}^\dagger$ to the column vector that corresponds to $|v=3\rangle$.

$$|v=3\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ \vdots \\ \vdots \\ \vdots \end{pmatrix} \begin{matrix} v=0 \\ 1 \\ 2 \\ 3 \end{matrix} \qquad \mathbf{a}^\dagger|v=3\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ \\ \end{pmatrix} \begin{matrix} v=0 \\ 1 \\ 2 \\ 3 \\ 4 \end{matrix}$$

D. (3 points) Is $\mathbf{a}^\dagger$ Hermitian?

$\mathbf{a}^\dagger$ is not Hermitian because

$$\mathbf{a}^\dagger_{v+1,v} = [v+1]^{1/2}$$

$$\mathbf{a}^\dagger_{v,v+1} = 0$$

$$\left(\mathbf{a}^\dagger_{v,v+1}\right)^* = 0^* = 0$$

Thus $\mathbf{a}^\dagger_{v+1,v} = \left(\mathbf{a}^\dagger_{v,v+1}\right)^*$

This is confusing because $(\mathbf{a}^\dagger)^* = \mathbf{a}$ and

$$(\mathbf{a}^\dagger)_{v+1,v} = (\mathbf{a}^\dagger)^*_{v,v+1} = (\mathbf{a})_{v,v+1} .$$

Extra credit for mention of this paradox.

E. (3 points) Is $(\mathbf{a}^\dagger + \mathbf{a})$ Hermitian? If it is, demonstrate it by the relationship between a matrix element that is the definition of a Hermitian operator.

$(\mathbf{a}^\dagger + \mathbf{a})$ is Hermitian because $(\mathbf{a}^\dagger + \mathbf{a})^* = (\mathbf{a} + \mathbf{a}^\dagger)$.

(i) Also $\mathbf{a}^\dagger + \mathbf{a} = \widetilde{X}$ and we know that $\widetilde{X}$ is Hermitian because expectation values of **X** are real, never complex or imaginary.

(ii) Also

$$\left(\mathbf{a}^\dagger + \mathbf{a}\right)_{v+1,v} = \mathbf{a}^\dagger_{v+1,v} + \mathbf{a}_{v+1,v} = (v+1)^{1/2} + 0$$

$$\left(\mathbf{a}^\dagger + \mathbf{a}\right)_{v,v+1} = \mathbf{a}^\dagger_{v,v+1} + \mathbf{a}_{v,v+1} = 0 + (v+1)^{1/2}$$

Since the matrix elements are real, the conjugate transpose of $(\mathbf{a}^\dagger + \mathbf{a})$ is $(\mathbf{a} + \mathbf{a}^\dagger)$.

F. (3 points) Is $i(\mathbf{a}^\dagger - \mathbf{a})$ Hermitian? If it is, use a matrix element relationship similar to what you used for part **E**.

$\tilde{p} = i(\mathbf{a}^\dagger - \mathbf{a})$

$\tilde{p}$ is Hermitian, thus i($\mathbf{a}^\dagger - \mathbf{a}$) is Hermitian.

Also

$$\left[i(\mathbf{a}^\dagger - \mathbf{a})\right]_{v+1,v} = i\mathbf{a}^\dagger_{v+1,v} - i\mathbf{a}_{v+1,v}$$

$$= i(v+1)^{1/2} - i0$$

$$\left[i(\mathbf{a}^\dagger - \mathbf{a})\right]^*_{v,v+1} = -i0 + i(v+1)^{1/2}$$

II. The Road to Quantum Beats (41 POINTS)

Consider the 3-level **H** matrix

$$\mathbf{H} = \hbar\omega \begin{pmatrix} 10 & 1 & 0 \\ 1 & 0 & 2 \\ 0 & 2 & -10 \end{pmatrix}$$

Label the eigen-energies and eigen-functions according to the dominant basis state character. The $\widetilde{10}$ state is the one dominated by the zero-order state with $E^{(0)} = 10$, $\tilde{0}$ by $E^{(0)} = 0$, and $-\widetilde{10}$ by $E^{(0)} = -10$.

A. (6 points) Use non-degenerate perturbation theory to derive the energies [HINT: $\mathbf{H}^{(0)}$ is diagonal, $\mathbf{H}^{(1)}$ is non-diagonal]:

(i) $E_{\widetilde{10}} = \boxed{10 + \frac{1^2}{10-0} = 10.1}$

(ii) $E_{\tilde{0}} = \boxed{0 + \frac{1^2}{0-10} + \frac{2^2}{0-(-10)} = 0 - \frac{1}{10} + \frac{4}{10} = \frac{3}{10}}$

(iii) $E_{-\widetilde{10}} = \boxed{-10 + \frac{4^2}{-10-0} = -10 - 1.6 = -11.6}$

B. (6 points) Use non-degenerate perturbation theory to derive the eigenfunctions [HINT: do not normalize]

(i) $\psi_{\widetilde{10}} = \psi_{10} + \frac{1}{10-0}\psi_0 = \psi_{10} + \frac{1}{10}\psi_0$

(ii) $\psi_{\tilde{0}} = \psi_0 + \frac{1}{0-10}\psi_{10} + \frac{2}{0-(-10)}\psi_{-10} = \psi_0 - \frac{1}{10}\psi_{10} + \frac{2}{10}\psi_{-10}$

(iii) $\psi_{-\widetilde{10}} = \psi_{-10} + \frac{2}{-10-0}\psi_0 = \psi_{-10} - \frac{2}{10}\psi_0$

C. (5 points) Demonstrate the *approximate* relationship: $\int \psi_{-\tilde{1}\tilde{0}} \mathbf{H} \psi_{-\tilde{1}\tilde{0}} dx \approx E_{-\tilde{1}\tilde{0}}$ [HINT: do not normalize].

$$\int \psi^*_{-\tilde{1}\tilde{0}} \mathbf{H} \psi_{-\tilde{1}\tilde{0}} dx = \int \left(\psi_{-10} - 0.2\psi_0\right)^* \mathbf{H} \left(\psi_{-10} - 0.2\psi_0\right) dx$$
$$= \mathbf{H}_{-10,-10} + 0.04\mathbf{H}_{0,0} - 0.2\mathbf{H}_{-10,0} - 0.2\mathbf{H}_{0,-10}$$
$$= -10 + 0 - (0.4)2 = -10.8$$
$$\int \psi_{-\tilde{1}\tilde{0}} \psi_{-\tilde{1}\tilde{0}} dx = \int \psi_{-\tilde{1}\tilde{0}} \psi_{-\tilde{1}\tilde{0}} dx + \left(\frac{2}{10}\right)^2 \int \psi_0 \psi_0 dx = 1 + 0.04 = 1.04$$

Normalized: $\frac{-10.8}{1.04} = -10.38$ which is closest to $E_{-\tilde{1}\tilde{0}} = -11.6$.

D. (8 points) Use the results from part **B** to write the elements of the $\mathbf{T}^\dagger$ matrix that non-degenerate perturbation theory promises will give a *nearly diagonal*

$$\tilde{\mathbf{H}} = \mathbf{T}^\dagger \mathbf{H} \mathbf{T}$$

matrix [do not normalize].

We know that $\mathbf{T}^\dagger \mathbf{H} \mathbf{T} = \widetilde{\mathbf{H}} = \begin{pmatrix} E_{\tilde{1}\tilde{0}} & 0 & 0 \\ 0 & E_{\tilde{1}\tilde{0}} & 0 \\ 0 & 0 & E_{-\tilde{1}\tilde{0}} \end{pmatrix}$

and that the columns of $\mathbf{T}^\dagger$ are the eigenvectors

$$\begin{matrix} \psi_{\tilde{1}\tilde{0}} & \psi_{\tilde{0}} & \psi_{-\tilde{1}\tilde{0}} \end{matrix}$$
$$\mathbf{T}^\dagger = \begin{pmatrix} 1 & -\frac{1}{10} & 0 \\ 0.1 & 1 & -0.2 \\ 0 & \frac{2}{10} & 1 \end{pmatrix} \begin{matrix} \psi_{10} \\ \psi_0 \\ \psi_{-10} \end{matrix}$$

E. (6 points) Suppose, at $t = 0$, you prepare a state $\Psi(x, 0) = \psi_0^{(0)}(x)$. Use the correct elements of the $\mathbf{T}^\dagger$ matrix to write $\Psi(x, 0)$ as a linear combination of the eigenstates, $\psi_{\tilde{1}\tilde{0}}, \psi_{\tilde{0}}$, and $\psi_{-\tilde{1}\tilde{0}}$ [do not normalize]:

We want one of the rows of $\mathbf{T}^\dagger$. We want the ψ_0 row $\Psi(x,0) = (0.1)\psi_{\tilde{1}\tilde{0}} + (1.0)\psi_{\tilde{0}} - 0.2\psi_{\tilde{1}\tilde{0}}$

F. (4 points) For the $\Psi(x,0) = c_{\tilde{1}\tilde{0}}\psi_{\tilde{1}\tilde{0}} + c_{\tilde{0}}\psi_{\tilde{0}} + c_{-\tilde{1}\tilde{0}}\psi_{-\tilde{1}\tilde{0}}$ initial state you derived in part **E**, write $\Psi(x, t)$ (do not normalize). If you do not believe your derived $c_{\tilde{1}\tilde{0}}$, $c_{\tilde{0}}$, and $c_{-\tilde{1}\tilde{0}}$ constants, leave them as symbols.

$$\Psi(x,t) = 0.1e^{-iE_{\tilde{1}\tilde{0}}t/\hbar}\psi_{\tilde{1}\tilde{0}} + 1.0e^{-iE_{\tilde{0}}t/\hbar}\psi_{\tilde{0}} - 0.2e^{-iE_{-\tilde{1}\tilde{0}}t/\hbar}\psi_{-\tilde{1}\tilde{0}}$$
$$= 0.1e^{-i(10.1)t/\hbar}\psi_{\tilde{1}\tilde{0}} + 1.0e^{-i(0.3)t/\hbar}\psi_{\tilde{0}} - 0.2e^{-i(-11.6)t/\hbar}\psi_{\tilde{1}\tilde{0}}$$

G. (6 points) If you obtained an answer you believe in part **G**, you will have discovered quantum beats. Even if you are not convinced that your answer to part **G** is correct, you will receive partial credit for being as explicit as you can be about $P_0(t)$:

(i) What is the value of $P_0(0)$?

$P_0(0) = 0$. You prepared $\psi(x,0) = \psi_0$ so $P_0(t = 0) = 1$.

(ii) The contribution of the zero-order $\psi_0^{(0)}$ state to the observed fluorescence will be modulated at some easily predicted frequencies. What are these frequencies?

The frequencies will be

$$\frac{\left(E_{\tilde{1}\tilde{0}} - E_{\tilde{0}}\right)}{\hbar}, \quad \frac{\left(E_{\tilde{1}\tilde{0}} - E_{-\tilde{1}\tilde{0}}\right)}{\hbar}, \quad \text{and} \quad \frac{\left(E_{\tilde{0}} - E_{-\tilde{1}\tilde{0}}\right)}{\hbar}$$

$$\frac{10.1 - 0.3}{\hbar} \qquad \frac{10.1 - (-11.6)}{\hbar} \qquad \frac{0.3 - (-11.6)}{\hbar}$$

$$\frac{9.8}{\hbar} \qquad \frac{21.7}{\hbar} \qquad \frac{11.9}{\hbar}$$

These are "quantum beats". You could also compute the amplitudes of each frequency, but that would be a tedious calculation.

III. Inter-Mode Anharmonicity in a Triatomic Molecule (10 POINTS)

Consider a nonlinear triatomic molecule. There are three vibrational normal modes, as specific in $\mathbf{H}^{(0)}$ and two anharmonic inter-mode interaction terms, as specified in $\mathbf{H}^{(1)}$.

$$\frac{\mathbf{H}^{(0)}}{hc} = \tilde{\omega}_1\left(\mathbf{N}_1 + 1/2\right) + \tilde{\omega}_2\left(\mathbf{N}_2 + 1/2\right) + \tilde{\omega}_3\left(\mathbf{N}_3 + 1/2\right)$$

$$\mathbf{H}^{(1)} = k_{122}Q_1Q_2^2 + k_{2233}Q_2^2Q_3^2$$

A. (2 points) List *all* of the (Δv_1, Δv_2, Δv_3) *combined* selection rules for nonzero matrix elements of the k_{122} term in $\mathbf{H}^{(1)}$? One of these selection rules is (+1, +2, 0).

The k_{122} term gives $\Delta v_1 = \pm 1$, $\Delta v_2 = 0, \pm 2$ and $\Delta v_3 = 0$. So we have

$(\Delta v_1, \Delta v_2, \Delta v_3) = (1,2,0)$

(1,0,0)

(1,–2,0)

(–1,2,0)

(–1,0,0)

(–1,–2,0)

B. (2 points) List *all* of the (Δv_1, Δv_2, Δv_3) selection rules for nonzero matrix elements of the k_{2233} term in $\mathbf{H}^{(1)}$?

The k_{2233} term gives $\Delta v_1 = 0$, $\Delta v_2 = \pm 2, 0$ and $\Delta v_3 = 0, \pm 2$. So now we have

$(\Delta v_1, \Delta v_2, \Delta v_3) = (0,2,2)$

(0,2,0)

(0,2,–2)

(0,0,2)

(0,0,0)

(0,0,–2)

(0,–2,2)

(0,–2,0)

0,–2,–2)

C. (2 points) In the table below, in the last column, place an X next to the inter-mode vibrational anharmonicity term to which the k_{2233} term contributes .

(i)	$\widetilde{\omega_e x_{e_{12}}}\left(v_1+1/2\right)\left(v_2+1/2\right)$	
(ii)	$\widetilde{\omega_e x_{e_{23}}}\left(v_2+1/2\right)\left(v_3+1/2\right)$	**X**
(iii)	$\widetilde{\omega_e z_{e_{2233}}}\left(v_2+1/2\right)^2\left(v_3+1/2\right)^2$	

We get $\omega_e x_{e_{23}}\left(v_2+1/2\right)\left(v_3+1/2\right)$ from $\mathbf{H}^{(1)}_{v_1,v_2,v_3;v_1,v_2,v_3} = E^{(1)}_{v_1,v_2,v_3}$. We also get contributions to this term from $E^{(2)}_{v_1,v_2,v_3}$.

D. (2 points) Does the term you specified in part **C** depend on the sign of k_{2233}?

The contributions from the $E^{(1)}_{v_1,v_2,v_3}$ term does depend on the sign of k_{2233} because there is a $(\Delta v_1, \Delta v_2, \Delta v_3) = (0, 0, 0)$ diagonal matrix element of $k_{2233}\mathbf{Q}_2^2\mathbf{Q}_3^2$.

E. (2 points) Does the k_{122} term in $\mathbf{H}^{(1)}$ give rise to any vibrational anharmonicity terms that are sensitive to the sign of k_{122}? Justify your answer.

The k_{122} term cannot give any vibrational anharmonicity terms that depend on the sign of k_{122} becaue of the $\Delta v_1 = \pm 1$ selection rule.

IV. Your First Encounter with a Non-Rigid Rotor (19 POINTS + 2 *extra credit*)

Your goal in this problem is to compute the *v*-dependence of the rotational constant of a harmonic oscillator.

Some equations that you will need:

$$B(R) = \frac{\hbar^2}{4\pi c\mu} R^{-2} \qquad , \qquad B_e = \frac{\hbar^2}{4\pi c\mu} R_e^{-2}$$

$$\hat{\mathbf{Q}} \equiv R - R_e = \left[\frac{\hbar}{4\pi c\mu\omega_e}\right]^{1/2} (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)$$

$$\frac{1}{R^2} = \frac{1}{(\mathbf{Q} + R_e)^2} = \frac{1}{R_e^2}\left(\frac{\mathbf{Q}}{R_e} + 1\right)^{-2}$$

Power series expansion:

$$\frac{1}{R^2} = \frac{1}{R_e^2}\left[1 - 2\left(\frac{\mathbf{Q}}{R_e}\right) + 3\left(\frac{\mathbf{Q}}{R_e}\right)^2 - 4\left(\frac{\mathbf{Q}}{R_e}\right)^3 + \ldots\right],$$

thus

$$B(R) = B_e\left[1 - 2\left(\frac{\mathbf{Q}}{R_e}\right) + 3\left(\frac{\mathbf{Q}}{R_e}\right)^2 - \ldots\right].$$

Some algebra yields

$$\boxed{\frac{\mathbf{Q}}{R_e} = \left(\frac{B_e}{\omega_e}\right)^{1/2} (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)} \qquad (1)$$

where $\left(\frac{B_e}{\omega_e}\right) \approx 10^{-3}$, an excellent order-sorting parameter.

$$\boxed{\hat{\mathbf{H}}^{\mathrm{ROT}} = hcB_e J(J+1)\left[1 - 2\left(\frac{B_e}{\omega_e}\right)^{1/2} (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger) + 3\left(\frac{B_e}{\omega_e}\right)(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^2 - \ldots\right]} \qquad (2)$$

A. (3 points) From boxed equation (2), what is $\hat{\mathbf{H}}^{(0)}$?

$\mathbf{H}^{(0)} = hcB_e J(J+1)$.

B. (3 points) What is $\hat{\mathbf{H}}^{(1)}$?

$$\mathbf{H}^{(1)} = hcB_e J(J+1)\left[-2\left(\frac{B_e}{\omega_e}\right)^{1/2}\left(\mathbf{a}+\mathbf{a}^{\dagger}\right)+3\left(\frac{B_e}{\omega_e}\right)\left(\mathbf{a}+\mathbf{a}^{\dagger}\right)^2+\ldots\right]$$

C. (6 points) $E_J = E_J^{(0)} + E_J^{(1)} + E_J^{(2)}$.

What is $E_J^{(0)}$, as a function of hc, B_e, and $J(J+1)$?

$$E_J^{(0)} = hcB_e J(J+1)$$

What is $E_J^{(1)}$, as a function of hc, B_e, ω_e, and $J(J+1)$?

$$E_{J,v}^{(1)} = hcB_e J(J+1)3\left(\frac{B_e}{\omega_e}\right)(2\mathbf{N}+1)$$

$$2\mathbf{N}+1 = 2(v+1/2)$$

D. (5 points) From experiment we measure

$$E_J = E_J^{(0)} + E_J^{(1)}$$

$$B_v = B_e - \alpha_e(v+1/2), \qquad B_{v+1} - B_v = -\alpha_e.$$

What is α_e expressed in terms of hc, B_e, and ω_e?

$$E_{J,v}^{(1)} = hcJ(J+1)(v+1/2)6B_e^2/\omega_e$$

$$\alpha_e = -6hcB_e^2/\omega_e$$

E. (2 points *extra credit*) Does the sign of α_e bother you? Why?

One might expect that as v increases, B_v will decrease. This is correct for an anharmonic non-rigid rotor. However, for a harmonic non-rigid rotor, B_v will increase with v. This occurs because $B(\mathbf{R})$ increases more at the inner turning point than it decreases at the outer turning point.

V. Derivation of One Part of the Angular Momentum Commutation Rule (10 POINTS)

$$\vec{\mathbf{L}} = \vec{\mathbf{r}} x \vec{\mathbf{p}} = \begin{pmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{pmatrix} = \hat{i}\left(yp_z - zp_y\right) - \hat{j}\left(xp_z - zp_x\right) + \hat{k}\left(xp_y - yp_x\right) \quad (1)$$

$$\left[\mathbf{x}, \mathbf{p}_x\right] = i\hbar \quad (2)$$

$$\left[\mathbf{L}_x, \mathbf{L}_y\right] = +\mathbf{i}\hbar\mathbf{L}_z \quad (3)$$

Use equations (1) and (2) to derive equation (3).

From Eq. (1) we have

$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

$$\left[L_x, L_y\right] = \left[yp_z - zp_y, zp_x - xp_z\right]$$

$$= \left[yp_z, zp_x\right] - \left[yp_z, xp_z\right] - \left[zp_y, zp_x\right] + \left[zp_y, xp_z\right]$$

$$= y\left[p_z, z\right]p_x - 0 - 0 + x\left[z, p_z\right]p_y$$

$[x, p_x] = i\hbar$

$$\left[L_x, L_y\right] = yp_x(-i\hbar) + xp_y(i\hbar)$$

$$= i\hbar\left[xp_y - yp_x\right]$$

but we know from Eq. (1) that $L_z = xp_y - yp_x$, thus $[L_x, L_y] = i\hbar L_z$ as required.

Some Possibly Useful Constants and Formulas

$h = 6.63 \times 10^{-34}$ J · s $\quad \hbar = 1.054 \times 10^{-34}$ J · s

$\varepsilon_0 = 8.854 \times 10^{-12} Cs^2 kg^{-1} m^{-3}$

$c = 3.00 \times 10^8$ m/s $\quad c = \lambda\nu \quad \lambda = h/p$

$m_e = 9.11 \times 10^{-31}$ kg $\quad m_H = 1.67 \times 10^{-27}$ kg

1 eV = 1.602 x 10^{-19} J $\quad e = 1.602$ x 10^{-19} C

$E = h\nu \quad a_0 = 5.29$ x 10^{-11} m $\quad e^{\pm i\theta} = \cos\theta \pm i\sin\theta$

$$\overline{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{where } R_H = \frac{me^4}{8\varepsilon_0^2 h^3 c} = 109{,}678 \text{ cm}^{-1}$$

Free particle:

$$E = \frac{\hbar^2 k^2}{2m} \qquad \psi(x) = A\cos(kx) + B\sin(kx)$$

Particle in a box:

$$E_n = \frac{h^2}{8ma^2} n^2 = E_1 n^2 \qquad \psi(0 \le x \le a) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right) \qquad n = 1, 2, \ldots$$

Harmonic oscillator:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad \text{[units of } \omega \text{ are radians/}s\text{]}$$

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}, \quad \psi_1(x) = \frac{1}{\sqrt{2}}\left(\frac{\alpha}{\pi}\right)^{1/4} \left(2\alpha^{1/2} x\right) e^{-\alpha x^2/2} \quad \psi_2(x) = \frac{1}{\sqrt{8}}\left(\frac{\alpha}{\pi}\right)^{1/4} \left(4\alpha x^2 - 2\right) e^{-\alpha x^2/2}$$

$$\hat{\tilde{x}} \equiv \sqrt{\frac{m\omega}{\hbar}}\hat{x} \qquad \hat{\tilde{p}} \equiv \sqrt{\frac{1}{\hbar m\omega}}\hat{p} \quad \text{[units of } \omega \text{ are radians/}s\text{]}$$

$$\mathbf{a} \equiv \frac{1}{\sqrt{2}}\left(\hat{\tilde{x}} + i\hat{\tilde{p}}\right) \qquad \frac{\hat{H}}{\hbar\omega} = \mathbf{a}\mathbf{a}^\dagger - \frac{1}{2} = \mathbf{a}^\dagger\mathbf{a} + \frac{1}{2} \qquad \hat{\mathbf{N}} = \mathbf{a}^\dagger\mathbf{a}$$

$$\mathbf{a}^\dagger = \frac{1}{\sqrt{2}}\left(\hat{\tilde{x}} - i\hat{\tilde{p}}\right)$$

$2\pi c\tilde{\omega} = \omega \qquad \text{[units of } \tilde{\omega} \text{ are cm}^{-1}\text{]}$

Semi-Classical

$\lambda = h/p$

$p_{\text{classical}}(x) = [2m(E - V(x))]^{1/2}$

period: $\tau = 1/\nu = 2\pi/\omega$

For a *thin* barrier of width ε where ε is very small, located at x_0, and height $V(x_0)$:

$$H_{nn}^{(1)} = \int_{x_0-\varepsilon/2}^{x_0+\varepsilon/2} \psi_n^{(0)*} V(x) \psi_n^{(0)} dx = \varepsilon V(x_0) \left| \psi_n^{(0)}(x_0) \right|^2$$

Perturbation Theory

$$E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$$

$$\psi_n = \psi_n^{(0)} + \psi_n^{(1)}$$

$$E_n^{(1)} = \int \psi_n^{(0)*} \widehat{H}^{(1)} \psi_n^{(0)} dx = H_{nn}^{(1)}$$

$$\psi_n^{(1)} = \sum_{m \neq n} \frac{H_{nm}^{(1)}}{E_n^{(0)} - E_m^{(0)}} \psi_m^{(0)}$$

$$E_n^{(2)} = \sum_{m \neq n} \frac{\left| H_{nm}^{(1)} \right|^2}{E_n^{(0)} - E_m^{(0)}}$$

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