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Example 1: The Slightly Anharmonic Oscillator

In Chapter 15, we discussed the diatomic molecule, a complicated many-body system. At low energies, however, we can neglect specific treatment of the electron degrees of freedom. The electron cloud can in first approximation be taken as the source of a potential binding the two atomic nuclei into a nearly rigid, vibrating structure. The position of the atomic nuclei of the diatomic molecule in 3-D space can be described by the three coordinates: r, the radial distance between the two atomic nuclei, and θ, and ϕ, the two angles describing the orientation of the molecule axis in our 3-D space. The electron cloud gives rise to a potential (see Fig. 22.1) with a deep minimum at $r = r_e$, where r_e is the equilibrium distance between the two nuclei. For very small values of r, the potential becomes strongly repulsive and rises to ∞. For very large values of r, the potential approaches a constant value of $V_{\text{diss.}}$. If we can raise the energy above this value, i.e., if $E > V_{\text{diss.}}$, the molecule will dissociate into two atomic fragments. For $E \ll V_{\text{diss.}}$, however, the potential will be nearly parabolic and can be expanded about the value $r = r_e$,

$$V(r) = V(r_e) + \frac{1}{2}\left(\frac{d^2V}{dr^2}\right)_{r_e}(r - r_e)^2 + \frac{1}{3!}\left(\frac{d^3V}{dr^3}\right)_{r_e}(r - r_e)^3 + \cdots \quad . \tag{1}$$

The Schrödinger equation for the wave function $\psi(r, \theta, \phi) = u(r)Y_{lm}(\theta, \phi)$ separates approximately (for the vibration–rotation perturbations, see problem 30) into a radial equation describing the vibration of the molecule and an angular equation describing the rotation of the molecule (see Chapter 15). The 1-D radial equation can be described by the Hamiltonian

$$H = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V(r). \tag{2}$$

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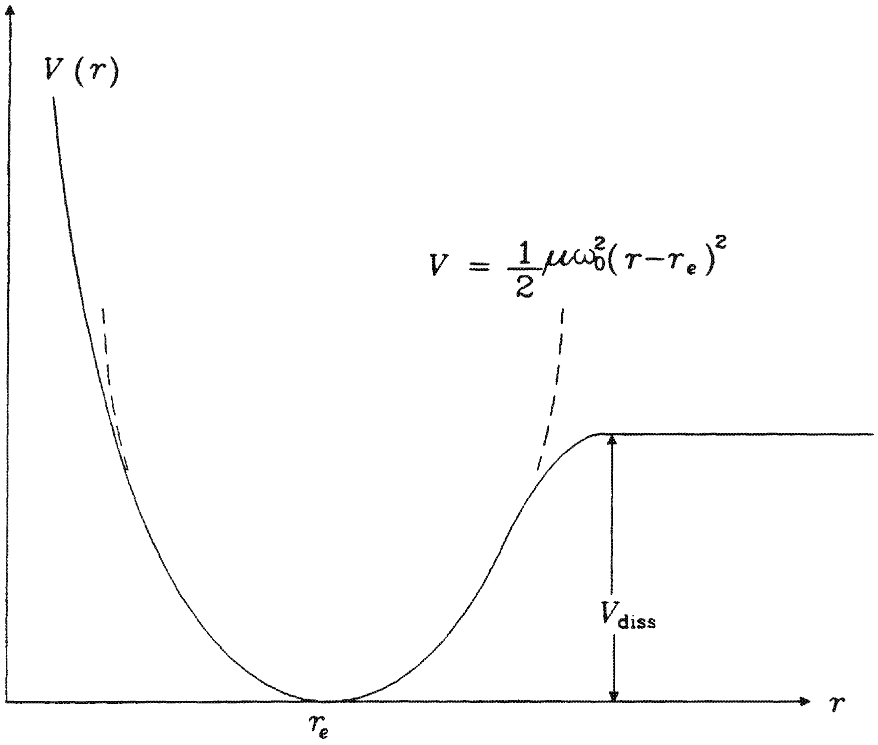

FIGURE 22.1. Diatomic molecule potential function.

For low-energy vibrational excitations, $V(r)$ can be approximated by the first few terms of the above Taylor expansion. Then, if we replace the vibrational coordinate, $(r - r_e)$, by a dimensionless coordinate, x,

$$(r - r_e) = \sqrt{\frac{\hbar}{\mu\omega_0}}x, \tag{3}$$

the vibrational Hamiltonian can be rewritten as

$$H = \hbar\omega_0\Big(\frac{1}{2}[-\frac{d^2}{dx^2} + x^2] + \lambda_3 x^3 + \lambda_4 x^4\Big), \tag{4}$$

with

$$\lambda_3 = \frac{1}{3!\hbar\omega_0}\left(\frac{\hbar}{\mu\omega_0}\right)^{\frac{3}{2}}\left(\frac{d^3V}{dr^3}\right)_{r_e}, \qquad \lambda_4 = \frac{1}{4!\hbar\omega_0}\left(\frac{\hbar}{\mu\omega_0}\right)^{2}\left(\frac{d^4V}{dr^4}\right)_{r_e}. \tag{5}$$

In most molecules $\lambda_3 \ll 1$, and $\lambda_4 \simeq$ order $(\lambda_3)^2$. Thus, we can write the Hamiltonian of eq. (4)

$$\begin{aligned} H &= H^{(0)} + \lambda H^{(1)} + \lambda^2 H^{(2)} \\ &= H^{(0)} + \hbar\omega_0\lambda_3 x^3 + \hbar\omega_0\lambda_4 x^4. \end{aligned} \tag{6}$$

The zeroth-order Hamiltonian is the simple 1-D harmonic oscillator Hamiltonian. Its eigenvectors are all nondegenerate, so we can use the machinery of stationary-state perturbation theory for an arbitrary nondegenerate state $|n\rangle$. We merely need to calculate the matrix elements of the two operators x^3 and x^4. These operators follow by matrix multiplication from the simple (known) matrix elements of x. Calculating first the matrix elements of x^2, we can use these together with the matrix elements of x to evaluate all needed matrix elements. We list some of the needed results, as follows:

$$\begin{aligned}
\langle n-2|x^2|n\rangle &= \tfrac{1}{2}\sqrt{n(n-1)} \\
\langle n+2|x^2|n\rangle &= \tfrac{1}{2}\sqrt{(n+1)(n+2)} \\
\langle n|x^2|n\rangle &= (n+\tfrac{1}{2}) \\
\langle m|x^2|n\rangle &= 0; \qquad \text{for} \quad m \neq n, (n \pm 2);
\end{aligned} \tag{7}$$

$$\begin{aligned}
\langle n-3|x^3|n\rangle &= \tfrac{1}{2}\sqrt{[n(n-1)(n-2)/2]} \\
\langle n+3|x^3|n\rangle &= \tfrac{1}{2}\sqrt{[(n+1)(n+2)(n+3)/2]} \\
\langle n-1|x^3|n\rangle &= \tfrac{3}{2}n\sqrt{[n/2]} \\
\langle n+1|x^3|n\rangle &= \tfrac{3}{2}(n+1)\sqrt{[(n+1)/2]} \\
\langle m|x^3|n\rangle &= 0; \qquad \text{for} \quad m \neq (n \pm 3), (n \pm 1).
\end{aligned} \tag{8}$$

Through second order, we shall only need the diagonal matrix element of x^4. This matrix element has the value

$$\langle n|x^4|n\rangle = \tfrac{3}{2}(n^2 + n + \tfrac{1}{2}). \tag{9}$$

The terms cubic in x have no diagonal matrix elements. Therefore, $H^{(1)}$ has no diagonal matrix element, and $E_n^{(1)} = 0$. The first correction to the energy is given by the second-order term

$$\begin{aligned}
\lambda^2 E_n^{(2)} &= \langle n^{(0)}|H^{(2)}|n^{(0)}\rangle + \sum_{k\neq n} \frac{|\langle k^{(0)}|H^{(1)}|n^{(0)}\rangle|^2}{(E_n^{(0)} - E_k^{(0)})} \\
&= \lambda_4 \langle n^{(0)}|\hbar\omega_0 x^4|n^{(0)}\rangle + \sum_{k\neq n} \frac{|\langle k^{(0)}|\lambda_3\hbar\omega_0 x^3|n^{(0)}\rangle|^2}{\hbar\omega_0(n-k)} \\
&= \lambda_4\hbar\omega_0\tfrac{3}{2}(n^2+n+\tfrac{1}{2}) + \frac{\lambda_3^2}{8}\hbar\omega_0\left(\frac{9n^3}{+1} + \frac{9(n+1)^3}{-1}\right. \\
&\qquad \left. + \frac{n(n-1)(n-2)}{+3} + \frac{(n+1)(n+2)(n+3)}{-3}\right).
\end{aligned} \tag{10}$$

The final result gives

$$\lambda^2 E_n^{(2)} = \hbar\omega_0\left[\tfrac{3}{2}\lambda_4(n^2+n+\tfrac{1}{2}) - \lambda_3^2(30n^2+30n+11)\right]. \tag{11}$$

We will also need the corrected state vectors. Often, it is sufficient to know these vectors to first order. For the slightly anharmonic oscillator, we have (to first order),

$$|n\rangle = |n^{(0)}\rangle + \lambda_3\left(\sum_{k\neq n}|k^{(0)}\rangle\frac{\langle k^{(0)}|x^3|n^{(0)}\rangle}{(n-k)}\right)$$

$$
\begin{aligned}
&= |n^{(0)}\rangle + \lambda_3\Bigg(|(n-3)^{(0)}\rangle \frac{\sqrt{n(n-1)(n-2)}}{6\sqrt{2}} \\
&\quad - |(n+3)^{(0)}\rangle \frac{\sqrt{(n+3)(n+2)(n+1)}}{6\sqrt{2}} \\
&\quad + |(n-1)^{(0)}\rangle \frac{3n\sqrt{n}}{2\sqrt{2}} - |(n+1)^{(0)}\rangle \frac{3(n+1)\sqrt{(n+1)}}{2\sqrt{2}}\Bigg). \qquad (12)
\end{aligned}
$$

These corrected state vectors will be needed to calculate the corrections to the transition probabilities. For a diatomic molecule, the electric dipole moment along the direction of the molecular symmetry axis can be given by

$$
\mu^{(el.)} = \mu_e + \left(\frac{d\mu}{dr}\right)_e (r - r_e) + \cdots = \mu_e + e_{\text{eff.}}\sqrt{\frac{\hbar}{\mu\omega_0}}\,x + \cdots\ , \qquad (13)
$$

where the dipole moment derivative is expressed in terms of an effective charge, $e_{\text{eff.}}$. Also, both the permanent electric dipole moment, μ_e, and the effective charge (which gives the strength of the dipole moment change during the harmonic oscillation) are zero for a homonuclear diatomic molecule, such as H_2, O_2, or N_2. Off-diagonal matrix elements of the electric dipole moment operator are given by

$$
\langle m^{(0)}|\mu^{(el.)}|n^{(0)}\rangle = \delta_{m(n\pm1)} e_{\text{eff.}}\sqrt{\frac{\hbar}{\mu\omega_0}}\langle m^{(0)}|x|n^{(0)}\rangle. \qquad (14)
$$

This equation leads to the zeroth-order vibrational selection rule, $\Delta n = \pm 1$ and a zeroth-order transition probability given by the Einstein A

$$
A_{n\rightarrow(n-1)} = \frac{8\pi\omega_0^3}{3hc^3} e_{\text{eff.}}^2 \frac{\hbar}{\mu\omega_0}\frac{n}{2}. \qquad (15)
$$

If first-order anharmonic corrections are included in the state vector, the vibrational selection rule $\Delta n = \pm 1$ is partially relaxed. For example, now transitions $n \rightarrow (n-2)$ may become possible. If we write the analog of eq. (12) for the bra $\langle (n-2)|$ through first order

$$
\begin{aligned}
\langle (n-2)| &= \langle (n-2)^{(0)}| + \lambda_3\Bigg(\langle (n-3)^{(0)}| \frac{3(n-2)\sqrt{(n-2)}}{2\sqrt{2}} \\
&\quad - \langle (n-1)^{(0)}| \frac{3(n-1)\sqrt{(n-1)}}{2\sqrt{2}} + \langle (n-5)^{(0)}| \frac{\sqrt{(n-2)(n-3)(n-4)}}{6\sqrt{2}} \\
&\quad - \langle (n+1)^{(0)}| \frac{\sqrt{(n+1)n(n-1)}}{6\sqrt{2}}\Bigg), \qquad (16)
\end{aligned}
$$

to first order in λ_3, the matrix element of $\langle (n-2)|x|n\rangle$ gets contributions from the zeroth-order component of $|n\rangle$ with the first-order components $\langle (n-1)^{(0)}|$ and $\langle (n+1)^{(0)}|$ of $\langle (n-2)|$, and from the zeroth-order component of $\langle (n-2)|$ with the first-order components $|(n-3)^{(0)}\rangle$ and $|(n-1)^{(0)}\rangle$ of $|n\rangle$, leading to

$$
\langle (n-2)|\mu^{(el.)}|n\rangle = e_{\text{eff.}}\sqrt{\frac{\hbar}{\mu\omega_0}}\lambda_3
$$

$$\begin{aligned}&\times\left(-\frac{3(n-1)\sqrt{(n-1)}}{2\sqrt{2}}\sqrt{\frac{n}{2}}-\frac{\sqrt{(n+1)n(n-1)}}{6\sqrt{2}}\sqrt{\frac{(n+1)}{2}}\right.\\&\left.+\frac{\sqrt{n(n-1)(n-2)}}{6\sqrt{2}}\sqrt{\frac{(n-2)}{2}}+\frac{3n\sqrt{n}}{2\sqrt{2}}\sqrt{\frac{(n-1)}{2}}\right)\\&=e_{\text{eff.}}\sqrt{\frac{\hbar}{\mu\omega_0}}\lambda_3\frac{1}{2}\sqrt{n(n-1)}.\end{aligned} \tag{17}$$

This equation leads to the transition probability given by the Einstein A

$$A_{n\to(n-2)}=\frac{8\pi(2\omega_0)^3}{3hc^3}e^2_{\text{eff.}}\frac{\hbar}{\mu\omega_0}\lambda_3^2\frac{n(n-1)}{4}. \tag{18}$$

This transition probability is weaker by a factor of λ_3^2 compared with the zeroth-order allowed transition $n \to (n-1)$.

A number of remarks are in order: (1) The formula given here for the transition probabilities is for the true 1-D anharmonic oscillator. It therefore assumes the diatomic molecule remains oriented in a specific direction in space, say, the x-direction in a crystalline environment. In a free diatomic molecule, say, in a gaseous sample in a microwave wave guide, the molecule is of course free to both rotate and vibrate. To get the transition probabilities, we would need the matrix elements of

$$\mu_x^{(el.)}=\mu_r\sin\theta\cos\phi,\qquad \mu_y^{(el.)}=\mu_r\sin\theta\cos\phi,\qquad \mu_z^{(el.)}=\mu_r\cos\theta, \tag{19}$$

with radial part, μ_r, given by eq. (13). The matrix elements given by eqs. (14) and (17) are just the radial (vibrational) part of the full electric dipole moment matrix element. This must be augmented by the angular (rotational) matrix elements of $\sin\theta\cos\phi$, $\sin\theta\sin\phi$, and $\cos\theta$. These matrix elements were actually evaluated in Chapter 9. These matrix elements lead to the rotational selection rule, $\Delta l = \pm 1$. Therefore, the actual transition in a free diatomic molecule involves both a change in vibrational quantum number, $\Delta n = \pm 1$, and a change in the rotational quantum number, $\Delta l = \pm 1$, leading to a vibration–rotation rather than to a pure vibrational transition.

(2): The actual numerical values of a vibrational transition probability, such as that given by eq. (15), is very small, corresponding to inverse times of the order of seconds or minutes, compared with an atomic electronic transition probability corresponding to lifetimes of the order of 10^{-8} seconds. Molecular vibrational or vibrational–rotational transitions are thus usually too weak to be seen in spontaneous emission. They are easily observed, however, in induced absorption processes, by placing the gaseous molecular sample in an electromagnetic beam of the appropriate infrared or microwave frequency. The transition probabilities will then be given by the Einstein B coefficients and the energy density of the incident beam. Because the Einstein B coefficients are proportional to the Einstein A coefficients, the results of this section will still be useful. Also, the induced emission probability for a transition $n \to (n-1)$ will be less than the induced absorption probability for the transition$(n-1) \to n$ if the number of molecules in the lower state, $N_{(n-1)}$, is greater than the number of molecules in the upper state, N_n, the usual situation for a gaseous sample in thermal equilibrium.