

Molecular structure: Diatomic molecules in the rigid rotor and harmonic oscillator approximations

Notes on Quantum Mechanics

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We have seen how the *adiabatic approximation* and the *Born-Oppenheimer approximation* allow us to get separate Schrödinger equations for the electronic and the nuclear coordinates.

The nuclear Schrödinger equation describes both the motion of the molecule as a whole through space and relative motion—vibrations and rotations—of the atoms that make up the molecule. The way to separate the motions through space from the internal motion is to reexpress the coordinates of each atom with respect to the laboratory in terms of (1) the three coordinates of the center of mass of the molecule and (2) the coordinates of each atom with respect to the center of mass.

This change of coordinates is illustrated most simply for the example of a diatomic molecule. The result is that the nuclear wave function factors into the product of (1) the wave function of the molecule moving freely through space, as a point mass centered at the center of mass of the molecule and with mass equal to the mass of the molecule, and (2) the wave function of the relative motion of the atoms with respect to the center of mass.

The Schrödinger equation for the relative motion of the atoms with respect to the center of mass depends on the details of the structure of the molecule. The simplest example, which we will explore here, is a diatomic molecule AB.

■ Transformation to center of mass and internal coordinates

In this case of a diatomic molecule AB the center of mass is at the point

$$R_{\text{cm}} = \frac{M_A R_A + M_B R_B}{M}$$

between the atoms, where $M = M_A + M_B$ is the total mass of the molecule, and the relative motion is described by the $R = R_A - R_B$. That is, the six coordinates, consisting of the three coordinates, $R_A = (X_A, Y_A, Z_A)$, of atom A and the three coordinates, $R_B = (X_B, Y_B, Z_B)$, of atom B, are replaced by the three coordinates, $R_{\text{cm}} = (X_{\text{cm}}, Y_{\text{cm}}, Z_{\text{cm}})$, of the center of mass, and the three coordinates, $R_{\text{rel}} = (X, Y, Z)$, of the relative motion with respect to the center of mass.

If we assume for simplicity that the molecule is confined in a cubical volume L^3 , then the Schrödinger equation for the center of mass is just the free particle Schrödinger equation. This means that the wave function for the motion of the molecule through space just the free particle wave function

$$\psi_{\text{cm}} = \left(\sqrt{\frac{2}{L}} \right)^3 \sin\left(\frac{n_x \pi X_{\text{cm}}}{L} \right) \sin\left(\frac{n_y \pi Y_{\text{cm}}}{L} \right) \sin\left(\frac{n_z \pi Z_{\text{cm}}}{L} \right),$$

and its contribution to the total energy is just

$$E_{\text{cm}} = \frac{\hbar^2}{8 M L^2} (n_x^2 + n_y^2 + n_z^2).$$

The Schrödinger equation for the relative motion about the center of mass is

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2} \right) + E_i(X, Y, Z) \right] \phi_i(X, Y, Z) = E_{\text{int}} \phi_i(X, Y, Z),$$

where $E_{\text{int}} = \mathcal{E} - E_{\text{cm}}$ is the contribution of the internal motion to the total energy \mathcal{E} , and

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

is the reduced mass of the molecule. We can actually simplify this Schrödinger equation somewhat by realizing that for a diatomic molecule the electronic eigenvalue, E_i , changes only when the separation between the two atoms changes. This means that E_i depends only on the internuclear distance,

$$E_i(X, Y, Z) = E_i(R),$$

and not at all on the orientation θ, ϕ of the axis in space. Note that now we (re-)use the symbol R to be

$$R = \sqrt{X^2 + Y^2 + Z^2}.$$

This simplification in turn means that we can separate the motion along the internuclear axis—the stretching and shrinking of R —from the rotation of the molecule about the center of mass by transforming to spherical polar internal coordinates,

$$(X, Y, Z) \rightarrow (R, \theta, \phi).$$

From our study of rotational motion and the one-electron atom we know that this means we can write the nuclear wave function as

$$\phi_i(X, Y, Z) = S_{k i}(R) Y_{J M}(\theta, \phi),$$

in terms of spherical harmonics and a wave function $S_{k i}(R)$ determined by the vibrational Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{R} \frac{d^2}{dR^2} R + \frac{\hbar^2 J(J+1)}{2\mu R^2} + E_i(R) \right] S_{k i}(R) = E_{\text{int}} S_{k i}(R).$$

The quantum number k indexes the number of loops in the wave function $S_{k i}(R)$ and the index i indicates the parametric dependence of wave function $S_{k i}(R)$ on the electronic potential curve, $E_i(R)$.

In a way analogous to what we did in the one-electron atom, we can define a related vibrational wave function

$$\chi_{k i}(R) = R S_{k i}(R)$$

to transform the vibrational Schrödinger equation into pure curvature form

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{\hbar^2 J(J+1)}{2\mu R^2} + E_i(R) \right] \chi_{k i}(R) = E_{\text{int}} \chi_{k i}(R).$$

■ The rigid rotor and harmonic oscillator approximations

A simple picture of a nuclear motion in a diatomic molecule is two masses connected by a spring. The masses can vibrate, stretching and compressing the spring with respect to the equilibrium spring length (the bond length). The masses can also rotate about the fixed point at the center of mass. The question arises whether the rotation can affect the vibration, say by stretching the spring. To answer this question, we can compare the expected frequencies of vibrational motion and rotational motion.

Now, we know that since molecules in an eigenstate do not move, we need to discuss motion in terms of wave packets. For vibrations, wave packets oscillate with at the harmonic (angular) frequency $\omega_{\text{vib}} = \sqrt{k/\mu}$. For rotations, the wave packets rotate with (angular) frequency roughly corresponding to the frequency

$$\omega_{\text{rot}} = \frac{\text{angular momentum}}{\text{moment of inertia}} \rightarrow \frac{\hbar \sqrt{J(J+1)}}{\mu R_e^2} \approx \frac{\hbar}{\mu R_e^2}.$$

As example, for N_2 ground state, $\tilde{\omega}_{\text{vib}} = 2358.5685 \text{ cm}^{-1}$, $R_e = 1.0976968 \text{ \AA}$, and for N-14 the reduced mass is 7.00153720 amu . These values give $\omega_{\text{vib}} = 7.07081 \times 10^{13} \text{ Hz}$ and $\omega_{\text{rot}} = 7.52781 \times 10^{11} \text{ Hz}$.

Verify these values for ω_{vib} and ω_{rot} .

The ratio of these values, $\omega_{\text{vib}}/\omega_{\text{rot}} = 93.9291$, means that the nitrogen molecule undergoes about 100 vibrations for each full rotation. This means that on average the molecule rotates at the midpoint of its vibrational excursion, namely at the internuclear distance R_e .

For this reason, it is a very good approximation is to assume that the rotational kinetic energy can be replaced by its value at the equilibrium internuclear distance, R_e .

$$\frac{\hbar^2 J(J+1)}{2\mu R^2} \rightarrow \frac{\hbar^2 J(J+1)}{2\mu R_e^2}.$$

This is known as the *rigid rotor approximation*. In this approximation the vibrational Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + E_i(R) \right] \chi_{ki}(R) = \left(E_{\text{int}} - \frac{\hbar^2 J(J+1)}{2\mu R_e^2} \right) \chi_{ki}(R).$$

The equilibrium internuclear distance is determined by the balance of attractive electron-nuclear forces, repulsive nuclear-nuclear forces, and repulsive electron-electron forces. We can simplify things further by expanding the electronic potential energy in a Taylor series with respect to the equilibrium separation,

$$E_i(R) = E_i(R_e) + \left(\frac{dE_i(R)}{dR} \right)_{R=R_e} (R - R_e) + \frac{1}{2} \left(\frac{d^2 E_i(R)}{dR^2} \right)_{R=R_e} (R - R_e)^2 + \dots$$

Since, by definition, $E_i(R)$ is a minimum at $R = R_e$, the second term in the series vanishes since the slope of $E_i(R)$ is zero at the minimum. If we also ignore the cubic and higher terms in the expansion, then we can write the electronic potential energy as

$$E_i(R) = E_i(R_e) + \frac{1}{2} \left(\frac{d^2 E_i(R)}{dR^2} \right)_{R=R_e} (R - R_e)^2.$$

This is known as the *harmonic oscillator approximation*. In this approximation the vibrational Schrödinger equation simplifies further to

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2} \left(\frac{d^2 E_i(R)}{dR^2} \right)_{R=R_e} (R - R_e)^2 \right] \chi_{ki}(R) \\ = \left(E_{\text{int}} - E_i(R_e) - \frac{\hbar^2 J(J+1)}{2\mu R_e^2} \right) \chi_{ki}(R).$$

This ‘simplified’ equation looks a little untidy. We can neaten it up in two ways.

First, the internal energy is the sum of contributions from electronic motion, vibrational motion, and electronic motion,

$$E_{\text{int}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}.$$

If we make the identifications

$$E_{\text{elec}} = E_i(R_e)$$

$$E_{\text{rot}} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2},$$

this means that the eigenvalue of the simplified vibrational Schrödinger equation is just E_{vib} , since

$$E_{\text{int}} - \left(E_i(R_e) + \frac{\hbar^2 J(J+1)}{2\mu R_e^2} \right) = (E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}) - (E_{\text{elec}} + E_{\text{rot}}) = E_{\text{vib}}.$$

Second, harmonic potential energy is expressed most naturally as $k\xi^2/2$, in terms of a force constant κ (Greek letter kappa) and displacement from equilibrium ξ (Greek letter xi). We can transform from the coordinate R to the displacement $\xi = R - R_e$ using $dR = d(\xi + R_e) = d\xi$. The result is the vibrational Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{d\xi^2} + \frac{1}{2} \kappa \xi^2 \right) \chi_{ki}(\xi) = E_{\text{vib}} \chi_{ki}(\xi),$$

where the force constant is

$$\kappa = \left(\frac{d^2 E_i(R)}{dR^2} \right)_{R=R_e}.$$

■ Grand summary of diatomic molecule molecular structure

Using the adiabatic and Born-Oppenheimer approximations, we express the molecular wave function and total energy as

$$\Psi_{\mathcal{E}}(R, r) \approx \psi_i(R, r) \phi_i(R) = \psi_i(R, r) \psi_{\text{cm}}(X_{\text{cm}}, Y_{\text{cm}}, Z_{\text{cm}}) \phi_i(X, Y, Z).$$

$$\mathcal{E} = E_{\text{cm}} + E_{\text{int}} = E_{\text{cm}} + E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}$$

The electronic wave function and energy are determined from

$$H_{\infty} \psi_i(R, r) = E_i(R) \psi_i(R, r),$$

using the infinite nuclear mass hamiltonian

$$H_{\infty} = -\frac{\hbar^2}{2m} \sum_e \nabla_e^2 + V(R, r).$$

The hamiltonian assumes the molecular center of mass is infinitely heavy.

The electronic energy, $E_i(R)$, contributes to the potential energy experienced by the nuclear motion, as described below.

The motion of the molecule through space, assumed to be bounded by a cubical volume L^3 , has wave function and energy

$$\psi_{\text{cm}}(X_{\text{cm}}, Y_{\text{cm}}, Z_{\text{cm}}) = \left(\sqrt{\frac{2}{L}} \right)^3 \sin\left(\frac{n_x \pi X_{\text{cm}}}{L} \right) \sin\left(\frac{n_y \pi Y_{\text{cm}}}{L} \right) \sin\left(\frac{n_z \pi Z_{\text{cm}}}{L} \right),$$

$$E_{\text{cm}} = \frac{\hbar^2}{8ML^2} (n_x^2 + n_y^2 + n_z^2), \quad n_x, n_y, n_z = 1, 2, 3, \dots$$

Using the rigid rotor and harmonic oscillator approximations, we express the wave function of internal nuclear motion (with respect to the center of mass) as

$$\phi_i(X, Y, Z) = \frac{\chi_{ki}(\xi)}{\xi} Y_{JM}(\theta, \phi),$$

where the harmonic oscillator wave function is determined from the Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{d\xi^2} + \frac{1}{2} \kappa \xi^2 \right) \chi_{ki}(\xi) = E_{\text{vib}} \chi_{ki}(\xi).$$

The internal energy,

$$E_{\text{int}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}},$$

is the sum of the electronic, vibrational and rotational contributions,

$$E_{\text{vib}} = h \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu}} \left(k - \frac{1}{2} \right), \quad \kappa = \left(\frac{d^2 E_i(R)}{dR^2} \right)_{R=R_e}, \quad k = 1, 2, 3, \dots,$$

$$E_{\text{elec}} = E_i(R_e),$$

$$E_{\text{rot}} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2}, \quad J = 0, 1, 2, \dots$$

These equations are a complete, approximate description of the quantum aspects of diatomic molecules. To test their correctness, the next step is to see how to use them to account for the structure and spectra of diatomic molecules.