

Vibration-Rotation in Many Dimensions

Yunting-Bu

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Outline

1 Triatomic Molecules

2 Tetraatomic Molecules

Triatomic Molecules

For a triatomic molecule, there are total of three sets of Jacobi coordinates.

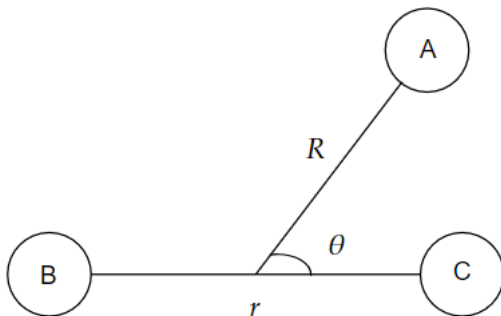


Figure: Jacobi coordinates

Triatomic Molecules

The kinetic energy operator is diagonal, and the triatomic Hamiltonian is given by the following

$$\begin{aligned} H &= -\frac{\hbar^2}{2\mu_R} \nabla_R^2 - \frac{\hbar^2}{2\mu_r} \nabla_r^2 + V(\mathbf{R}, \mathbf{r}) \\ &= \frac{\hbar^2}{2\mu_R} \frac{1}{R} \frac{\partial^2}{\partial R^2} R + \frac{\mathbf{L}^2}{2\mu_R R^2} - \frac{\hbar^2}{2\mu_r} \frac{1}{r} \frac{\partial^2}{\partial r^2} r + \frac{\mathbf{j}^2}{2\mu_r r^2} + V(\mathbf{R}, \mathbf{r}) \end{aligned} \quad (1)$$

where \mathbf{L} and \mathbf{j} are the orbital and diatomic angular momentum operators. Here the reduced masses are defined by

$$\mu_r = \frac{m_B m_C}{m_B + m_C} \quad (2)$$

$$\mu_R = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C} \quad (3)$$

Triatomic Molecules

Since the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{j}$ is conserved, we can use an angular momentum basis in the coupled-angular momentum representation to expand the wavefunction. There are two equivalent and widely used representation: the space-fixed(SF) or body-fixed(BF) representation. In the SF, the basis functions are eigenfunctions of (J^2, J_Z, j^2, L^2) operators where J_Z is the projection of \mathbf{J} along the space-fixed Z axis. In the BF representation, the basis function chosen are eigenfunctions of (J^2, J_Z, j^2, J_z) operators where L^2 is replaced by the projection of \mathbf{J} along the body-fixed z axis.

Usually, the body-fixed z axis is chosen to be along the vector \mathbf{R} . In this choice of BF frame, the projection of \mathbf{J} along the BF z axis is the same as that of \mathbf{j} because \mathbf{L} has zero projection along the \mathbf{R} axis.

Triatomic Molecules

We choose to use the BF. A general multidimensional expansion of eigenfunctions of a triatomic molecule $\psi(\mathbf{R}, \mathbf{r})$ can be written as

$$\psi^{JMp}(\mathbf{R}, \mathbf{r}) = \sum_{n\nu jK} C_{n\nu jK} \frac{u_n(R)}{R} \frac{\phi_\nu(r)}{r} \mathcal{Y}_{jK}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}) \quad (4)$$

where J and M are the quantum numbers of the total momentum and its space-fixed Z component, respectively, and p is the parity of the system. The function $u_n(R)$ and $\phi_\nu(r)$ are basis functions for two radial coordinates R and r .

The parity-adapted BF angular momentum eigenfunction is defined as

$$\mathcal{Y}_{jK}^{JMp} = \frac{1}{\sqrt{2(1 + \delta_{K0})}} [\mathcal{Y}_{jK}^{JM} + (-1)^P \mathcal{Y}_{j-K}^{JM}] \quad (5)$$

where the total parity is $P = (-1)^{J+p}$ and \mathcal{Y}_{jK}^{JMp} is the product of a normalized rotation matrix and an associated Legendre polynomial

$$\mathcal{Y}_{jK}^{JM} = \tilde{D}_{MK}^J P_{jK} \quad (6)$$

The BF angular momentum eigenfunctions are also eigenfunctions of the total parity P in which the $(2J + 1)$ -manifold of K states is split into a $(K + 1)$ -manifold of K states with $K = 0, 1, 2, \dots, J$ for even total parity ($P=\text{even}$) and a K -manifold of K states with $K = 1, 2, \dots, J$ for odd total parity ($P=\text{odd}$).

Next we need to construct the Hamiltonian matrix \mathbf{H} which is the sum of the kinetic energy and potential matrices

$$\mathbf{H} = \mathbf{T}_R + \mathbf{T}_r + \mathbf{V} + \mathbf{V}_R^c + \mathbf{V}_r^c \quad (7)$$

For simplicity, we assume that all the basis functions are orthogonal. Thus the kinetic energy matrices are given by

$$[\mathbf{T}_R]_{n\nu jK, n'\nu' j'K'} = \langle u_n | -\frac{\hbar^2}{2\mu_R} \frac{d^2}{dR^2} | u_{n'} \rangle \delta_{\nu\nu'} \delta_{jj'} \delta_{KK'} \quad (8)$$

$$[\mathbf{T}_r]_{n\nu jK, n'\nu' j'K'} = \langle \phi_\nu | -\frac{\hbar^2}{2\mu_r} \frac{d^2}{dr^2} | \phi_{\nu'} \rangle \delta_{nn'} \delta_{jj'} \delta_{KK'} \quad (9)$$

Triatomic Molecules

By utilizing the orthogonality property of the BF angular momentum functions and the fact that the potential V depends only on three internal coordinates (R, r, θ) , we can evaluate the potential matrix as

$$[\mathbf{V}]_{n\nu jK, n'\nu' j'K'} = \langle u_n \phi_\nu P_{jK} | V | P_{j'K} \phi_{\nu'} u_{n'} \rangle \delta_{KK'} \quad (10)$$

We note that the potential matrix is diagonal in the BF (K) representation.

The potential matrix \mathbf{V}_r^c is simply given by

$$[\mathbf{V}_r^c]_{n\nu jK, n'\nu' j'K'} = \langle \phi_n u | \frac{\hbar^2}{2\mu_r r^2} | \phi_{\nu'} \rangle j(j+1) \delta_{nn'} \delta_{jj'} \delta_{KK'} \quad (11)$$

However, the evaluation of the centrifugal potential matrix \mathbf{V}_R^c in BF representation is a little more tricky. First, the orbital angular momentum is expressed as

$$L^2 = (\mathbf{J} - \mathbf{j})^2 = J^2 + j^2 - 2J_z j_z - J_+ j_- - J_- j_+ \quad (12)$$

Triatomic Molecules

We can readily write out the result for the full matrix element of the centrifugal potential in the body-fixed frame

$$\begin{aligned} [\mathbf{V}_{\mathbf{r}}^{\mathbf{c}}]_{n\nu jK, n'\nu' j'K'} &= \frac{\hbar^2}{2\mu_R R^2} \langle n\nu jK | (\mathbf{J} - \mathbf{j})^2 | n'\nu' j'K' \rangle \\ &= \delta_{\nu\nu'} \delta_{jj'} \langle u_n | \frac{\hbar^2}{2\mu_R R^2} | u_{n'} \rangle W_{KK'}^{Jj} \end{aligned} \quad (13)$$

where the matrix element $W_{KK'}^{Jj}$ is defined by

$$\begin{aligned} W_{KK'}^{Jj} &= [J(J+1) + j(j+1) - 2K^2] \delta_{KK'} - \lambda_{JK}^+ \lambda_{jK}^+ \sqrt{1 + \delta_{K0}} \delta_{K+1, K'} \\ &\quad - \lambda_{JK}^- \lambda_{jK}^- \sqrt{1 + \delta_{K1}} \delta_{K-1, K'} \end{aligned} \quad (14)$$

where

$$\lambda_{JK}^{\pm} = \sqrt{J(J+1) - K(K \pm 1)} \quad (15)$$

$$\lambda_{jK}^{\pm} = \sqrt{j(j+1) - K(K \pm 1)} \quad (16)$$

CS approximation

In the BF representation, the interaction potential is diagonal while the centrifugal potential is tridiagonal in the K states. In other words, the coupling of different K states is caused by the centrifugal potential, not the interaction potential. This is the main reason for the popular use of the BF representation because it is often a good approximation to simply neglect the K -coupling to arrive at diagonal representation of the Hamiltonian in the quantum number K .

$$[\mathbf{V}_{\mathbf{r}}^{\mathbf{c}}]_{n\nu j K, n'\nu' j' K'} \approx \delta_{\nu\nu'} \delta_{KK'} \langle u_n | \frac{\hbar^2}{2\mu_R R^2} | u_{n'} \rangle \times [J(J+1) + j(j+1) - 2K^2] \quad (17)$$

The neglect of centrifugal coupling is called the CS (centrifugal sudden or coupled states) approximation.

Tetraatomic Molecules: Hamiltonian and Basis

If we use the Jacobi coordinates shown in figure

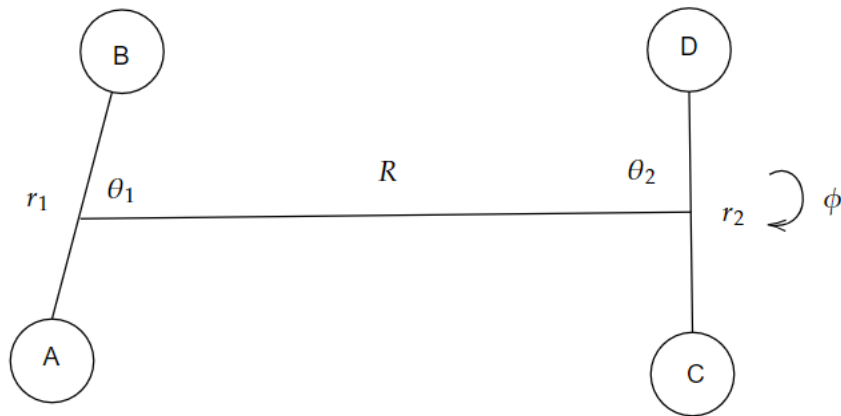


Figure: Jacobi coordinates

Hamiltonian and Basis

The Hamiltonian can be written as

$$\begin{aligned} H &= -\frac{\hbar^2}{2\mu_R} \nabla_R^2 - \frac{\hbar^2}{2\mu_1} \nabla_{r_1}^2 - \frac{\hbar^2}{2\mu_2} \nabla_{r_2}^2 + V(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2) \\ &= -\frac{\hbar^2}{2\mu_R} \frac{1}{R} \frac{\partial^2}{\partial R^2} R + \frac{\mathbf{L}^2}{2\mu_R R^2} - \frac{\hbar^2}{2\mu_1} \frac{1}{r_1} \frac{\partial^2}{\partial r_1^2} r_1 + \frac{\mathbf{j}_1^2}{2\mu_1 r_1^2} \\ &\quad - \frac{\hbar^2}{2\mu_2} \frac{1}{r_2} \frac{\partial^2}{\partial r_2^2} r_2 + \frac{\mathbf{j}_2^2}{2\mu_2 r_2^2} + V(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2) \end{aligned} \quad (18)$$

Now we have three angular momentum operators ($\mathbf{L}, \mathbf{j}_1, \mathbf{j}_2$) that are coupled to form the total angular momentum \mathbf{J} which is conserved.

Hamiltonian and Basis

The method of choosing suitable basis sets to expand the wavefunction is essentially similar to that of triatomic systems. For example, we can expand the wavefunction as

$$\psi^{JM\epsilon}(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2, t) = \sum_{n\nu jK} C_{n\nu jK} \frac{u_n(R)}{R} \frac{\phi_\nu(r_1, r_2)}{r_1 r_2} \mathcal{Y}_{j_{12}K}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \quad (19)$$

Here we have used the composite indexes ν and j to denote collections of quantum numbers, i.e., $\nu = (\nu_1 \nu_2)$ and $j = (j_1, j_2, j_{12})$ in order to simplify notation. The double vibrational basis $\phi_\nu(r_1, r_2)$ is defined as

$$\phi_\nu(r_1, r_2) = \phi_{\nu_1}(r_1) \phi_{\nu_2}(r_2) \quad (20)$$

and $\mathcal{Y}_{j_{12}K}^{JMp}$ is the parity-adapted BF angular momentum basis function.

Hamiltonian and Basis

It can be shown that the operation of the parity operator on the nonparity-adapted BF angular momentum basis yields the result

$$\hat{p}\mathcal{Y}_{j_{12}K}^{JMp} = (-1)^{j_1+j_2+j_{12}+J}\mathcal{Y}_{j_{12}-K}^{JMp} \quad (21)$$

Thus we can define $\mathcal{Y}_{j_{12}K}^{JMp}$ by

$$\mathcal{Y}_{j_{12}K}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \frac{1}{\sqrt{2(1 + \delta_{K0})}} \left[\mathcal{Y}_{j_{12}K}^{JMp} + (-1)^{P+j_1+j_2+j_{12}}\mathcal{Y}_{j_{12}-K}^{JMp} \right] \quad (22)$$

where P is the total parity.

The BF basis

$$\mathcal{Y}_{j_{12}K}^{JMp}(\hat{\mathbf{R}}, \hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \tilde{D}_{KM}^J \mathcal{Y}_{j_1 j_2}^{j_{12}K} \quad (23)$$

where the normalization rotation matrix and Euler angles remain the same as for triatomics. The BF internal angular momentum function $\mathcal{Y}_{j_1 j_2}^{j_{12}K}$ is defined as

$$\begin{aligned} \mathcal{Y}_{j_1 j_2}^{j_{12}K}(\theta_1, \theta_2, \phi) = & \sqrt{2\pi} \sum_{m_1} \langle j_1 m_1 j_2 K - m_1 | j_{12} K \rangle \\ & \times Y_{j_1 m_1}(\theta_1, 0) Y_{j_2 K - m_1}(\theta_2, \phi) \end{aligned} \quad (24)$$

where Y_{jm} are spherical harmonics and ϕ_{12} is the out-of-plane torsional angles.

Hamiltonian and Basis

The kinetic energy matrices are simple to evaluate and the treatment is not repeated here. The potential matrix in the angular basis for fixed radial coordinates (R, r_1, r_2) can be calculated similarly to the case for triatomic molecules

$$\begin{aligned} V^{JK}_{jj'}(R, r_1, r_2) &= \langle JMjK | V | JMj'K' \rangle \\ &= \sum_{m_1, m'_1} \langle j_1 m_1 j_2 K - m_1 | j_{12} K \rangle \langle j'_1 m'_1 j'_2 K - m'_1 | j'_{12} K \rangle \\ &\quad \times \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 P_{j_1 m_1}(\theta_1) P_{j_2 K - m_1}(\theta_2) \\ &\quad \times V_{m_1, m'_1}(R, r_1, r_2, \theta_1, \theta_2) P_{j'_1 m'_1}(\theta_1) P_{j'_2 K - m'_1}(\theta_2) \end{aligned} \quad (25)$$

where

$$V_{m_1, m'_1} = \frac{1}{\pi} \int_0^\pi d\phi \cos[(m_1 - m'_1)\phi] V(R, r_1, r_2, \theta_1, \theta_2, \phi) \quad (26)$$

The matrix element of the centrifugal potential can be calculated by a formula similar to that for triatomic molecules

$$\begin{aligned} V_{K,K'}^{cJj} &= \frac{\hbar^2}{2\mu R^2} \langle JMjK | (\mathbf{J} - \mathbf{j}_{12})^2 | JMj'K' \rangle \\ &= \frac{\hbar^2}{2\mu R^2} \delta_{jj'} W_{KK'}^{Jj_{12}} \end{aligned} \quad (27)$$

where $W_{KK'}^{Jj_{12}}$ is defined in (14) with the replacement of j by j_{12}

Hamiltonian and Basis

The full Hamiltonian matrix can now be constructed from separate pieces and has the following form

$$\begin{aligned} H_{n\nu j K, n' \nu' j' K'}^J &= \langle JM n \nu j K | H | JM n' \nu' j' K' \rangle \\ &= \left[\langle u_n | T_R | u_{n'} \rangle \delta_{\nu \nu'} + \langle \phi_\nu | T_{r_1} + T_{r_2} + \frac{\hbar^2}{2\mu_1 r_1^2} j_1(j_1 + 1) \right. \\ &\quad \left. + \frac{\hbar^2}{2\mu_{r_2} r_2^2} j_2(j_2 + 1) | \phi_{\nu'} \rangle \delta_{nn'} \right] \delta_{jj'} \delta_{KK'} \\ &\quad + V_{n\nu j, n' \nu' j'}^{JK} \delta_{KK'} + V_{nK, n' K'}^{cJj} \delta_{\nu \nu'} \delta_{jj'} \end{aligned} \quad (28)$$

where T_R , T_{r_1} and T_{r_2} are the kinetic energy operators corresponding to the R , r_1 and r_2 radial coordinates in the Hamiltonian.

Hamiltonian and Basis

Here the full potential matrices are calculated from the angular part by

$$V_{n\nu j, n'\nu' j'}^{JK} = \langle u_n \phi_\nu | V_{j, j'}^{JK} | \phi_{\nu'} u_{n'} \rangle \quad (29)$$

and

$$V_{nK, n'K'}^{cJj} = \langle u_n | V_{K, K'}^{cJj} | u_{n'} \rangle \quad (30)$$

The bound state problem is then solved by diagonalizing the Hamiltonian matrix, provided that the size of the matrix is not prohibitively large.

Symmetry for Two Identical Monomers

if AB and CD are identical monomers as in $(\text{HF})_2$, the rovibrational eigenfunctions $X_{\nu j K}^{JMp} = \mathcal{Y}_{jK}^{JMp} \phi_\nu$ should be properly symmetrized. The symmetrized rovibrational basis can be written as

$$X_{\nu j K}^{\pm JMp} = \left[2 \left(1 \pm \langle X_{\nu j K}^{JMp} | \hat{p}_{ex} | X_{\nu j K}^{JMp} \rangle \right) \right]^{-1/2} \left[X_{\nu j K}^{JMp} \pm \hat{p}_{ex} X_{\nu j K}^{JMp} \right] \quad (31)$$

where \hat{p}_{ex} is the exchange operator that changes the coordinates $(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) \rightarrow (\mathbf{r}_2, \mathbf{r}_1, -\mathbf{R})$. It can be shown that

$$\hat{p}_{ex} X_{\nu j K}^{JMp} = (-1)^{p+j_{12}} X_{\tilde{\nu} \tilde{j} K}^{JMp} \quad (32)$$

where $\tilde{\nu}$ and \tilde{j} denote transposed indexes (j_2, j_1, j_{12}) and (ν_2, ν_1) .

Symmetry for Two Identical Monomers

Thus the symmetrized basis is

$$X_{\nu j K}^{\pm J M p} = \Delta_{\nu j, \tilde{\nu} \tilde{j}} \left[\mathcal{Y}_{j K}^{J M p} \Phi_{\nu} \pm (-1)^{j_{12}+p} \mathcal{Y}_{\tilde{j} K}^{J M p} \Phi_{\tilde{\nu}} \right] \quad (33)$$

where the normalized constant is given by

$$\Delta_{\nu j, \tilde{\nu} \tilde{j}} = [2(1 + \delta_{\nu \tilde{\nu}} \delta_{j \tilde{j}})]^{-1/2} = [2(1 + \delta_{\nu_1 \nu_2} \delta_{j_1 j_2})]^{-1/2} \quad (34)$$

Here we note that quantum numbers ν and j are restricted by the requirement of $\nu_1 \geq \nu_2$ and $j_1 \geq j_2$ for $\nu_1 = \nu_2$. Note that for $\nu_1 = \nu_2$ and $j_1 = j_2$, the allowed j_{12} quantum numbers must satisfy the condition $p_{ex}(-1)^{j_{12}+p} = 1$.

Symmetry for Two Identical Monomers

The potential matrix elements in the symmetrized basis representation $X_{\nu j K}^{\pm J M p}$ can be written explicitly in terms of unsymmetrized functions

$$\begin{aligned} \langle X_{\nu j K}^{\pm J M p} | V | X_{\nu' j' K'}^{\pm J M p} \rangle = & 2 \Delta_{\nu j, \tilde{\nu} \tilde{j}} \Delta_{\nu' j', \tilde{\nu}' \tilde{j}'} \delta_{K K'} \left[\mathcal{Y}_{j K}^{J M p} | V_{\nu \nu'} | \mathcal{Y}_{j' K'}^{J M p} \right. \\ & \left. \pm (-1)^{j_{12}+p} \langle \mathcal{Y}_{\tilde{j} K}^{J M} | V_{\tilde{\nu} \nu'} | \mathcal{Y}_{j' K'}^{J M p} \rangle \right] \end{aligned} \quad (35)$$

where

$$V_{\nu \nu'} = \langle \phi_{\nu} | V | \phi_{\nu'} \rangle \quad (36)$$

and

$$V_{\tilde{\nu} \nu'} = \langle \phi_{\tilde{\nu}} | V | \phi_{\nu'} \rangle \quad (37)$$

The centrifugal potential in the symmetrized basis representation is given by

$$\begin{aligned} \langle X_{\nu j K}^{\pm J M p} | V_c | X_{\nu' j' K'}^{\pm J M p} \rangle = \\ \Delta_{\nu j, \tilde{\nu} \tilde{j}} \Delta_{\nu' j', \tilde{\nu}' \tilde{j}'} \frac{\hbar^2}{\mu R^2} \left[\delta_{\nu \nu'} \delta_{j j'} \pm (-1)^{j_{12}+p} \delta_{\tilde{\nu} \nu'} \delta_{\tilde{j} j'} \right] W_{K, K'}^{J j_{12}}, \end{aligned} \quad (38)$$