

## CHAPTER 4

## The Molecular Energy Eigenstates

## 4.1 The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation provides a simplification of the molecular Hamiltonian based on the large difference in nuclear and electronic masses. Electrons are light and move much faster than the nuclei, thus we can effectively consider the nuclei fixed and calculate the motion of the electrons in the Coulomb field of the nuclei.

Consider a molecule consisting of  $N$  electrons,  $P$  nuclei with charges  $Z_p$  and masses  $M_p$ . The Hamiltonian for this system is

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \frac{\hbar^2}{2} \sum_{p=1}^P \left( \frac{1}{M_p} \right) \nabla_p^2 - \sum_{i=1}^N \sum_{p=1}^P \frac{Z_p e^2}{r_{pi}} + \sum_{p>q}^P \frac{Z_p Z_q e^2}{R_{pq}} + \sum_{i>j}^N \frac{e^2}{r_{ij}}$$

$$= T_e + T_N + V(N-e) + V(N-N) + V(e-e),$$

which can be rearranged as

$$H = \left[ -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_p \sum_i \frac{Z_p e^2}{r_{pi}} + \sum_{i>j} \frac{e^2}{r_{ij}} \right] + \left[ -\frac{\hbar^2}{2} \sum_{p=1}^P \left( \frac{1}{M_p} \right) \nabla_p^2 + \sum_{p>q} \frac{Z_p Z_q e^2}{R_{pq}} \right],$$

where the terms in the first brackets include both electronic and nuclear coordinates and those in the last set of brackets are purely nuclear.

## 4.2 Adiabatic Born-Oppenheimer Approximation

In the adiabatic Born-Oppenheimer approximation, the wavefunction,  $\Psi(\vec{R}_p, \vec{r}_i)$ , is separated into an electronic part,  $\phi(\vec{r}_i, \vec{R}_p)$ , and a nuclear part  $\chi(\vec{R}_p)$ , where the electronic part depends parametrically on the nuclear coordinates,

$$\Psi(\vec{R}_p, \vec{r}_i) = \chi(\vec{R}_p) \phi(\vec{r}_i, \vec{R}_p).$$

The time-independent Schrödinger equation,

$$H\Psi = E\Psi,$$

becomes

$$\begin{aligned} & \left[ -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_p \sum_i \frac{Z_p e^2}{r_{pi}} + \sum_{i>j}^N \frac{e^2}{r_{ij}} \right] \chi(\vec{R}_p) \phi(\vec{r}_i, \vec{R}_p) \\ & + \left[ -\frac{\hbar^2}{2} \sum_{p=1}^P \left( \frac{1}{M_p} \right) \nabla_p^2 + \sum_{p>q} \frac{Z_p Z_q e^2}{R_{pq}} \right] \chi(\vec{R}_p) \phi(\vec{r}_i, \vec{R}_p) = E \chi(\vec{R}_p) \phi(\vec{r}_i, \vec{R}_p), \end{aligned}$$

where we realize that  $\nabla_i^2$  acts only on the electronic coordinates  $\vec{r}_i$ , and  $\nabla_q^2$  acts only on  $\vec{R}_q$ , *i.e.*, consider

$$\nabla_i^2 \left\{ \chi(\vec{R}_q) \phi(\vec{r}_i, \vec{R}_q) \right\} = \chi(\vec{R}_q) \nabla_i^2 \left\{ \phi(\vec{r}_i, \vec{R}_q) \right\}$$

and also

$$\begin{aligned} & \nabla_q^2 \left\{ \chi(\vec{R}_q) \phi(\vec{r}_i, \vec{R}_q) \right\} = \vec{\nabla}_q \cdot \left\{ \phi(\vec{r}_i, \vec{R}_q) \vec{\nabla}_q \chi(\vec{R}_q) + \chi(\vec{R}_q) \vec{\nabla}_q \phi(\vec{r}_i, \vec{R}_q) \right\} \\ & = \phi(\vec{r}_i, \vec{R}_q) \nabla_q^2 \chi(\vec{R}_q) + \vec{\nabla}_q \phi(\vec{r}_i, \vec{R}_q) \cdot \vec{\nabla}_q \chi(\vec{R}_q) + \vec{\nabla}_q \chi(\vec{R}_q) \cdot \vec{\nabla}_q \phi(\vec{r}_i, \vec{R}_q) + \chi(\vec{R}_q) \nabla_q^2 \phi(\vec{r}_i, \vec{R}_q) \\ & = \phi(\vec{r}_i, \vec{R}_q) \nabla_q^2 \chi(\vec{R}_q) + 2 \vec{\nabla}_q \chi(\vec{R}_q) \cdot \vec{\nabla}_q \phi(\vec{r}_i, \vec{R}_q) + \chi(\vec{R}_q) \nabla_q^2 \phi(\vec{r}_i, \vec{R}_q) \end{aligned}$$

Thus, using this result the Schrödinger equation becomes

$$\begin{aligned} & \chi(\vec{R}_q) \left[ -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{i,q} \frac{Z_q e^2}{r_{qi}} + \sum_{i>j}^N \frac{e^2}{r_{ij}} \right] \phi(\vec{r}_i, \vec{R}_q) + \phi(\vec{r}_i, \vec{R}_q) \left[ -\frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \nabla_q^2 + \sum_{q>p} \frac{Z_q Z_p e^2}{R_{qp}} \right] \chi(\vec{R}_q) \\ & + \left\{ -\frac{\hbar^2}{2} \sum_q \frac{2}{M_q} \vec{\nabla}_q \chi(\vec{R}_q) \cdot \vec{\nabla}_q \phi(\vec{r}_i, \vec{R}_q) - \chi(\vec{R}_q) \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \nabla_q^2 \phi(\vec{r}_i, \vec{R}_q) \right\} = E \chi(\vec{R}_q) \phi(\vec{r}_i, \vec{R}_q), \end{aligned}$$

where the first term in brackets depends only on the electronic coordinates if we assume the nuclei are fixed in position; the second term in brackets depends only on the nuclear coordinates. The third term on the left side couples the electronic and nuclear coordinates. If we actually fix the nuclei, then all derivatives of  $\chi(\vec{R}_q)$  and  $\phi(\vec{r}_i, \vec{R}_q)$  with respect to the nuclear coordinates, *i.e.*, terms involving  $\vec{\nabla}_q$  and  $\nabla_q^2$  vanish.

From the above equation, we see a less harsh approximation that still allows a separation of variables. That is, only the terms in  $\{\dots\}$  need to be neglected. If we neglect the  $\{\dots\}$ , then the Schrödinger equation becomes

$$\begin{aligned} \frac{1}{\phi(\vec{r}_i, \vec{R}_q)} \left[ -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,q} \frac{Z_q e^2}{r_{qi}} + \sum_{i>j}^N \frac{e^2}{r_{ij}} \right] \phi(\vec{r}_i, \vec{R}_q) \\ + \frac{1}{\chi(\vec{R}_q)} \left[ -\frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \nabla_q^2 + \sum_{q>p} \frac{Z_q Z_p e^2}{R_{qp}} \right] \chi(\vec{R}_q) = E, \end{aligned}$$

or equivalently,

$$\begin{aligned} \frac{1}{\phi(\vec{r}_i, \vec{R}_q)} \left[ -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,q} \frac{Z_q e^2}{r_{qi}} + \sum_{i>j}^N \frac{e^2}{r_{ij}} \right] \phi(\vec{r}_i, \vec{R}_q) \\ = -\frac{1}{\chi(\vec{R}_q)} \left[ -\frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \nabla_q^2 + \sum_{q>p} \frac{e^2 Z_q Z_p}{R_{qp}} \right] \chi(\vec{R}_q) + E = E_e(\vec{R}_q) \end{aligned}$$

Therefore the variables are separated and we have two equations to solve, one for  $\chi(\vec{R}_q)$  and one for  $\phi(\vec{r}_i, \vec{R}_q)$ . They are

$$\left[ -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{q=1}^P \frac{Z_q e^2}{r_{qi}} + \sum_{i>j}^N \frac{e^2}{r_{ij}} \right] \phi(\vec{r}_i, \vec{R}_q) = E_e(\vec{R}_q) \phi(\vec{r}_i, \vec{R}_q)$$

for the electronic motion, and

$$\left[ -\frac{\hbar^2}{2} \sum_{q=1}^P \frac{1}{M_q} \nabla_q^2 + \sum_{q>p}^P \frac{Z_q Z_p e^2}{R_{qp}} \right] \chi(\vec{R}_q) = (E - E_e(\vec{R}_q)) \chi(\vec{R}_q)$$

for the nuclear motion. We define the energy of the nuclear motion,  $E_N$ , by

$$E - E_e(\vec{R}_q) = E_N,$$

thus, the total energy is

$$E = E_N + E_e.$$

If we can rearrange the Schrödinger equation for the nuclear motion, we get

$$\left[ -\frac{\hbar^2}{2} \sum_{q=1}^P \frac{1}{M_q} \nabla_q^2 + \sum_{q>p}^P \frac{Z_q Z_p e^2}{R_{qp}} + E_e(\vec{R}_q) \right] \chi(\vec{R}_q) = E \chi(\vec{R}_q).$$

This equation says that the electronic energy (as a function of the nuclear coordinates) acts like a potential energy term for the nuclear motion. That is, the electronic energy surface,  $E_e(\vec{R}_q)$ , is part of the potential in which the nuclei move. In fact, it provides the attractive part of the total potential energy.  $E_e(\vec{R}_q)$  is obtained by fixing the nuclei at arbitrary positions  $\vec{R}_q = \vec{R}_{0q}$  (held fixed) and solving the electronic motion equation given above.

Notice that it is just as valid (and more useful) to write the full Schrödinger equation as

$$\begin{aligned} \frac{1}{\phi(\vec{r}_i, \vec{R}_q)} \left[ -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{i,q}^{N,P} \frac{Z_q}{r_{qi}} + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{q>p}^P \frac{Z_q Z_p e^2}{r_{qp}} \right] \phi(\vec{r}_i, \vec{R}_q) \\ = -\frac{1}{\chi(\vec{R}_q)} \left[ -\frac{\hbar^2}{2} \sum_{q=1}^P \frac{1}{M_q} \nabla_q^2 \right] \chi(\vec{R}_q) + E = E'_e(\vec{R}_q) \end{aligned}$$

Giving instead the two slightly different equations

$$\left[ -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{i,q}^{N,P} \frac{Z_q}{r_{qi}} + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{q>p}^P \frac{Z_q Z_p e^2}{r_{qp}} \right] \phi(\vec{r}_i, \vec{R}_q) = E'_e(\vec{R}_q) \phi(\vec{r}_i, \vec{R}_q),$$

where the factor in brackets is called the *electronic Hamiltonian*, and

$$\left[ -\frac{\hbar^2}{2} \sum_{q=1}^P \frac{1}{M_q} \nabla_q^2 + E'_e(\vec{R}_q) \right] \chi(\vec{R}_q) = E \chi(\vec{R}_q),$$

where the terms in the brackets make up the *nuclear Hamiltonian*. All we have done is to move the nuclear repulsion term into the electronic part where it acts like a constant for the fixed nuclei. We will usually expand  $E'_e(\vec{R}_q)$  in a Taylor series as (dropping the prime and using primes to indicate derivatives

$$\begin{aligned} E_e(\vec{R}_q) &= E_e(Q_K) = E_e(0) + \sum_K Q_K E'_e(0) + \sum_{K,L} Q_K Q_L E''_e(0) \\ &= E_e(0) + \sum_K \cancel{Q_K} E'_e(0) + \sum_K Q_K^2 E''_e(0), \end{aligned}$$

where the second term vanishes for the equilibrium positions of the nuclei, *i.e.*,  $Q_K = 0, \forall K$ . In the expansion, we have switched from Cartesian coordinates of the nuclei,  $\vec{R}_q$ , to the normal coordinates of the molecule,  $Q_K$ .

For the procedure to be valid, the neglected terms that allowed us to separate the motions of the nuclei and electrons must be small, *i.e.*,

$$-\hbar^2 \sum_{q=1}^P \frac{1}{M_q} \vec{\nabla}_q \chi(\vec{R}_q) \cdot \vec{\nabla}_q \phi(\vec{r}_i, \vec{R}_q) - \chi(\vec{R}_q) \frac{\hbar^2}{2} \sum_{q=1}^P \frac{1}{M_q} \nabla_q^2 \phi(\vec{r}_i, \vec{R}_q)$$

must be negligible compared to other terms, as for example,

$$\left[ + \frac{\hbar^2}{2} \phi(\vec{r}_i, \vec{R}_q) \sum_{q=1}^P \frac{1}{M_q} \nabla_q^2 \chi(\vec{R}_q) \right].$$

This is usually true, because  $\phi(\vec{r}_i, \vec{R}_q)$  is a slowly varying function of nuclear coordinates.

To examine the adiabatic Born-Oppenheimer approximation further, we consider the electronic Hamiltonian,

$$H_e = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i \sum_q \frac{Z_q e^2}{r_{qi}} + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{q>p} \frac{Z_q Z_p e^2}{r_{qp}}$$

with the electronic Schrödinger equation,

$$H_e \phi_k(\vec{r}_i, \vec{R}_q) = E_e^k(\vec{R}_q) \phi_k(\vec{r}_i, \vec{R}_q),$$

and the nuclear Hamiltonian is

$$H_n = E_e^k(\vec{R}_q) - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \nabla_q^2$$

with the nuclear wavefunctions given by the solutions of

$$\left( E_e^k(\vec{R}_q) - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \nabla_q^2 \right) \chi_k(\vec{R}_q) = E_n \chi_k(\vec{R}_q).$$

However, we need the complete solutions to the Schrödinger equation

$$H\psi = E\psi,$$

where  $H$  is the complete non-relativistic Hamiltonian,

$$H = H_e - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \nabla_q^2.$$

We assume solutions of the form

$$\psi = \sum_k c_k \phi_k(\vec{r}_i, \vec{R}_q) \chi_k(\vec{R}_q)$$

*i.e.*, a linear combination of products of approximate electronic and nuclear wavefunctions. Then,

$$H\psi = \left( H_e - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \nabla_q^2 \right) \sum_k c_k \phi_k(i, q) \chi_k(q) = E\psi.$$

Multiplying on the left by  $\phi_l^*$  and integrating over the electronic coordinate gives

$$\begin{aligned} \int \phi_l^* H \psi d\vec{r}_i &= \sum_k c_k \left[ \langle \phi_l | H_e | \phi_k \rangle \chi_k(q) - \frac{\hbar^2}{2} \left\langle \phi_l \left| \sum_q \frac{1}{M_q} \nabla_q^2 \right| \phi_k \right\rangle \chi_k(q) \right] \\ &= \sum_k c_k \left[ \delta_{kl} E_e^l(q) \chi_k(q) - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \langle \phi_l | \nabla_q^2 | \phi_k \rangle \chi_k(q) \right] \\ &= \sum_k c_k \left[ \delta_{kl} E_e^l(q) \chi_k(q) - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \langle \phi_l | \{ |\phi_k(i, q)\rangle \nabla_q^2 \chi_k(q) \right. \\ &\quad \left. + 2 |\vec{\nabla}_q \phi_k(i, q)\rangle \cdot \vec{\nabla}_q \chi(q) + |\nabla_q^2 \phi_k(i, q)\rangle \chi(q) \} \right] \\ &= \sum_k c_k \left[ \delta_{kl} E_e^l(q) - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \left\{ \delta_{kl} \nabla_q^2 + 2 \langle \phi_l | \vec{\nabla}_q | \phi_k(i, q) \rangle \cdot \vec{\nabla}_q + \langle \phi_l | \nabla_q^2 | \phi_k \rangle \right\} \right] \chi_k(q) \\ &= E \langle \phi_l | \phi_k \rangle \chi_k(q) \end{aligned}$$

Therefore, we obtain

$$\begin{aligned} \sum_k c_k \left[ \delta_{kl} \left( E_e^l(q) - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} - E \right) - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \langle \phi_l | \vec{\nabla}_q | \phi_k \rangle \cdot \vec{\nabla}_q - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \langle \phi_l | \nabla_q^2 | \phi_k \rangle \right] \chi_k(q) &= 0 \\ c_l \left[ E_e^l(q) - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \nabla_q^2 - E \right] \chi_k(q) + \sum_k c_k \left( -\frac{\hbar^2}{2} \sum_q \frac{2}{M_q} \langle \phi_l | \vec{\nabla}_q | \phi_k \rangle \cdot \vec{\nabla}_q + \langle \phi_l | \nabla_q^2 | \phi_k \rangle \right) \chi_k(q) &= 0 \end{aligned}$$

Now, let's define (primes do not indicate derivatives here)

$$E'_{lk}(q) = -\frac{\hbar^2}{2} \sum_p \frac{1}{M_p} \langle \phi_l | \nabla_p^2 | \phi_k \rangle$$

$$\bar{E}''_{lk}{}^p(q) = -\frac{\hbar^2}{2} \frac{2}{M_p} \langle \phi_l | \bar{\nabla}_p | \phi_k \rangle,$$

then

$$c_l \left[ E'_e(q) - \frac{\hbar^2}{2} \sum_q \frac{1}{M_q} \nabla_q^2 - E \right] \chi_l(q) + \sum_k c_k \left[ \sum_p \bar{E}''_{lk}{}^p(q) \cdot \bar{\nabla}_p + E'_{lk}(q) \right] \chi_k(q) = 0$$

$$c_l \left[ -\frac{\hbar^2}{2} \sum_p \frac{1}{M_p} \nabla_q^2 + E_l(q) + \sum_p \bar{E}''_{ll}{}^p(q) \cdot \bar{\nabla}_p + E'_{ll}(q) \right] \chi_l(q) = -\sum_{k \neq l} \left[ \sum_p \bar{E}''_{lk}{}^p(q) \cdot \bar{\nabla}_p + E'_{lk}(q) \right] \chi_k(q) c_k$$

For real functions,  $\phi_l$ ,

$$E''_{ll}(q) = 0,$$

and we have

$$c_l \left[ -\frac{\hbar^2}{2} \sum_p \frac{1}{M_p} \nabla_q^2 + E_l(q) + \sum_p \bar{E}''_{ll}{}^p(q) \cdot \bar{\nabla}_p + E'_{ll}(q) - E \right] \chi_l(q) = -\sum_{k \neq l} c_k \left[ \sum_p \bar{E}''_{lk}{}^p(q) \cdot \bar{\nabla}_p + E'_{lk}(q) \right] \chi_k(q)$$

We have the Born-Oppenheimer approximation, if we assume

$$E'_{kl}(q) = 0$$

and

$$\bar{E}''_{lk}{}^p(q) = 0$$

for all  $l$  and  $k$ . In this case,

$$c_l \left[ -\frac{\hbar^2}{2} \sum_p \frac{1}{M_p} \nabla_q^2 + E_l(q) - E \right] \chi_l(q) = 0$$

$$\left[ -\frac{\hbar^2}{2} \sum_p \frac{1}{M_p} \nabla_q^2 + E_l(q) \right] \chi_l(q) = E \chi_l(q)$$

For the adiabatic Born-Oppenheimer approximation,

$$E'_{lk}(q) = 0 \quad l \neq k$$

$$\bar{E}''_{lk}{}^p(q) = 0 \quad l \neq k$$

and we have

$$c_l \left[ -\frac{\hbar^2}{2} \sum_p \frac{1}{M_p} \nabla_q^2 + E_l(q) + E'_{ll}(q) - E \right] \chi_l(q) = 0$$

$$\left[ -\frac{\hbar^2}{2} \sum_p \frac{1}{M_p} \nabla_q^2 + V_l(q) - E \right] \chi_l(q) = 0$$

where  $V_l(q) = E_l(q) + E'_{ll}(q)$ . Finally, for the non-adiabatic Born-Oppenheimer approximation all  $E'_{lk}$  and  $\bar{E}''_{lk}{}^p \neq 0$ . For computational purposes, the crude Born-Oppenheimer approximation is preferred.

#### 4.3 The Crude Born-Oppenheimer Approximation

As before, the molecular Hamiltonian is

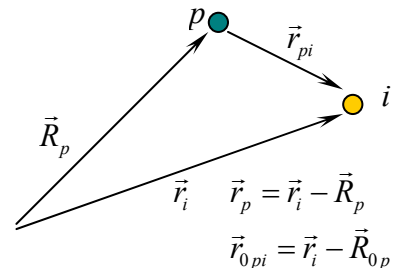
$$H = \left[ \frac{-\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_p \sum_{i=1}^N \frac{Z_p e^2}{r_{pi}} + \sum_{i>j}^N \frac{e^2}{r_{ij}} \right] + \left[ \frac{-\hbar^2}{2} \sum_{p=1}^P \left( \frac{1}{M_p} \right) \nabla_p^2 + \sum_{p>q}^P \frac{Z_p Z_q e^2}{R_{pq}} \right].$$

This time, however, we assume solutions of the form

$$\psi(\vec{r}_i, \vec{R}_p) = \phi(\vec{r}_i) \chi(\vec{R}_p).$$

Substituting into the time-independent Schrödinger equation,

$$H\psi = E\psi,$$



we get

$$\begin{aligned} \chi(\vec{R}_p) \left( -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 \right) \phi(\vec{r}_i) - \sum_{q=1}^P \sum_{i=1}^N \frac{Z_q e^2}{r_{qi}} \chi(\vec{R}_p) \phi(\vec{r}_i) + \chi(\vec{R}_p) \sum_{i>j} \frac{e^2}{r_{ij}} \phi(\vec{r}_i) \\ + \phi(\vec{r}_i) \left( -\frac{\hbar^2}{2} \sum_{q=1}^P \frac{1}{M_q} \nabla_q^2 + \sum_{q>p} \frac{Z_q Z_p e^2}{R_{pq}} \right) \chi(\vec{R}_p) = E \chi(\vec{R}_p) \phi(\vec{r}_i) \end{aligned}$$

Except for the second term on the left-hand side of the equation, the nuclear and electronic motions are separable. Because of the large difference in the electronic and nuclear masses it is reasonable to fix the nuclei and solve for the electronic states of the 0<sup>th</sup> order Hamiltonian,

$$H_0^e = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_p \sum_i \frac{Z_p e^2}{r_{opi}} + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{p>q} \frac{Z_p Z_q e^2}{R_{pq}}.$$

This is just the equation one solves in a single-point molecular orbital calculation (with CI).

The nuclear coordinate dependence comes in through the terms,

$$-\sum_{q=1}^P \sum_{n=1}^N \frac{Z_q e^2}{r_{qi}} + \sum_{q>p} \frac{Z_q Z_p e^2}{R_{pq}}.$$

These potential energy terms contain all of the nuclear coordinate dependence of the Hamiltonian, and they can be expanded in a Taylor series about the zero point in the above equation, which is taken to be the equilibrium geometry of the molecule in the ground state. That is,

$$H^e = H_0^e(q_i, Q=0) + \sum_{K=1}^{3P} Q_K \left( \frac{\partial H^e}{\partial Q_K} \right)_{Q=0} + \frac{1}{2} \sum_{K,L=1}^{3P} Q_K Q_L \left( \frac{\partial^2 H^e}{\partial Q_K \partial Q_L} \right)_{Q=0} + \dots,$$

where we have made a coordinate transformation to a set of coordinates that are zero at the equilibrium positions of the nuclei ( $Q=0$ ) in the ground electronic state  $g$  and, generally, involve motions of all of the nuclei.  $H^e$  is the full Hamiltonian of the molecule except for the kinetic energy of the nuclei,

$$-\frac{\hbar^2}{2} \sum_{K=1}^{3P} \frac{1}{\mu_K} \frac{\partial^2}{\partial Q_K^2},$$

expressed in the new coordinates, where  $\mu_K$  is the reduced mass of the coordinate  $Q_K$ . We will later show that the kinetic energy can be written in this form when the  $Q_K$  are the normal coordinates. This is not obvious. Thus, the mixing coordinate systems since we will ultimately solve parts of the problem independently, the full Hamiltonian can be written as

$$H = \left[ -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_p \sum_i \frac{Z_p e^2}{r_{0_{pi}}} + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{p>q} \frac{Z_p Z_q e^2}{R_{0_{pq}}} \right] + \left[ \sum_{K=1}^{3P-6} Q_K \left( \frac{\partial H}{\partial Q_K} \right)_{Q=0} + \frac{1}{2} \sum_{L,K=1}^{3P-6} Q_K Q_L \left( \frac{\partial^2 H}{\partial Q_K \partial Q_L} \right)_{Q=0} + \dots \right] + \left[ -\frac{\hbar^2}{2} \sum_{K=1}^{3P-6} \frac{1}{\mu_K} \frac{\partial^2}{\partial Q_K^2} \right],$$

where the first term in brackets is just  $H_0^e(q_i, Q=0)$ .

#### 4.4 The Electronic States

In this expression, we have separated the Hamiltonian into three terms, the first has the nuclei fixed and only the electrons move. This term gives the usual molecular orbital problem. We assume we can solve this problem at least approximately for the electronic states,  $|l_\nu(\vec{r}_i)\rangle$ , with energies,  $E_{l_\nu}^0$ , which satisfy

$$H_0^e |l_\nu(\vec{r}_i)\rangle = E_{l_\nu}^0 |l_\nu(\vec{r}_i)\rangle,$$

giving the 0<sup>th</sup> order molecular energy eigenstates with 0<sup>th</sup> order energies  $E_{l_\nu}^0$ . Here,  $\nu$  is a subscript that runs over all degenerate states with energy  $E_{l_\nu}^0$ . The second term couples the electronic and nuclear motion and we treat it as a perturbation.

#### 4.5 Vibrational States (Harmonic Oscillator)

We now consider the vibrational motion problem, which we solve in terms of the normal coordinates for the electronic ground electronic state, for which we have from the solution of the electronic states

$$|l_\nu\rangle = |g\rangle,$$

which satisfies

$$H_0^e |g\rangle = E_g^0 |g\rangle.$$

The 0<sup>th</sup> order solution to the full Schrödinger equation (both  $Q_K$  and  $q_i$  dependent) is the product state,

$$\psi(\vec{r}_i, \vec{R}_p) = |g\rangle |\chi(Q_K)\rangle.$$

If we let the full molecular Hamiltonian operate on this 0<sup>th</sup> order molecular state, we obtain

$$H\psi(\vec{r}_i, \vec{R}_p) = H|g\rangle|\chi_n(Q_K)\rangle = (H^e + T_N)|g\rangle|\chi_n\rangle.$$

If we now multiply on the left by  $\langle g|$  and integrate over the electronic coordinates, we have for the right side of the equation,

$$\left(\langle g|H^e|g\rangle + T_N \langle g|g\rangle\right)|\chi_n\rangle,$$

where,

$$\langle g|H^e|g\rangle = \langle g|H_0^e|g\rangle + \sum_{K=1}^{3N} Q_K \left\langle g \left| \left( \frac{\partial H^e}{\partial Q_K} \right)_0 \right| g \right\rangle + \frac{1}{2} \sum_{K,L=1}^{3N} Q_K Q_L \left\langle g \left| \left( \frac{\partial^2 H^e}{\partial Q_K \partial Q_L} \right)_0 \right| g \right\rangle + \dots$$

Truncating the series, we have the approximate expression,

$$\langle g|H^e|g\rangle \approx E_g^0 + \sum_K Q_K \left\langle g \left| \left( \frac{\partial H^e}{\partial Q_K} \right)_0 \right| g \right\rangle + \frac{1}{2} \sum_K \sum_L Q_K Q_L \left\langle g \left| \left( \frac{\partial^2 H^e}{\partial Q_K \partial Q_L} \right)_0 \right| g \right\rangle.$$

So we have,

$$\begin{aligned} \left(\langle g|H^e|g\rangle + T_N \langle g|g\rangle\right)|\chi_n\rangle = \\ \left[ E_g^0 + \sum_K Q_K \left\langle g \left| \left( \frac{\partial H^e}{\partial Q_K} \right)_0 \right| g \right\rangle + \frac{1}{2} \sum_K \sum_L Q_K Q_L \left\langle g \left| \left( \frac{\partial^2 H^e}{\partial Q_K \partial Q_L} \right)_0 \right| g \right\rangle + T_N \right] |\chi_n\rangle \end{aligned}$$

Now, since we assumed that the coordinates  $Q_K$  are the normal coordinates, the linear term must vanish because the Taylor expansion is about the equilibrium position of the nuclei. That is, the slope at the bottom of the potential well in which the nuclei move must be zero. Said another way “expanding about the equilibrium position” means there can be no force on the nuclei at  $Q_1 = 0, \dots, Q_K = 0, \dots$ . Thus, the force given by

$$F_K = -\frac{\partial E_g(Q_K)}{\partial Q_K}$$

must vanish for all  $K$  at the equilibrium point.

$$0 = F_L = -\frac{\partial}{\partial Q_L} \left( E_g^0 + \sum_K Q_K \left\langle g \left| \left( \frac{\partial H}{\partial Q_K} \right)_0 \right| g \right\rangle + \frac{1}{2} \sum_K Q_K^2 \left\langle g \left| \left( \frac{\partial^2 H}{\partial Q_K^2} \right)_0 \right| g \right\rangle \right)$$

$$= - \left\langle \mathbf{g} \left| \left( \frac{\partial H}{\partial Q_K} \right)_0 \right| \mathbf{g} \right\rangle - Q_L \left\langle \mathbf{g} \left| \left( \frac{\partial^2 H}{\partial Q_L^2} \right)_0 \right| \mathbf{g} \right\rangle$$

at  $Q_L = 0$ , the force will vanish if and only if we have

$$\left\langle \mathbf{g} \left| \left( \frac{\partial H}{\partial Q_L} \right)_0 \right| \mathbf{g} \right\rangle = 0, \quad \forall L.$$

In the above we have also used the fact that the quadratic term

$$\frac{1}{2} \sum_{K,L} Q_K Q_L \left\langle \mathbf{g} \left| \left( \frac{\partial^2 H}{\partial Q_K \partial Q_L} \right)_0 \right| \mathbf{g} \right\rangle$$

is diagonal in the normal coordinate system, and we write this term for the ground electronic state as

$$\frac{1}{2} \sum_{K,L} Q_K Q_L \left\langle \mathbf{g} \left| \left( \frac{\partial^2 H}{\partial Q_K \partial Q_L} \right)_0 \right| \mathbf{g} \right\rangle = \frac{1}{2} \sum_K Q_K^2 f_K,$$

where the  $f_K$  are the force constants of a harmonic oscillator,

$$f_K = \left\langle \mathbf{g} \left| \left( \frac{\partial^2 H}{\partial Q_K^2} \right)_0 \right| \mathbf{g} \right\rangle.$$

Thus, finally we have

$$\left( \langle \mathbf{g} | H^e | \mathbf{g} \rangle + T_N \langle \mathbf{g} | \mathbf{g} \rangle \right) | \chi_n \rangle = \left[ T_N + E_g^0 + \frac{1}{2} \sum_K Q_K^2 f_K \right] | \chi_n \rangle$$

Summarizing, the potential in which the nuclei move in the ground electronic state is the harmonic potential

$$E_g(Q_K) = E_g^0 + \frac{1}{2} \sum_K Q_K^2 f_K.$$

(We must still show that a set of coordinates  $Q_K$  can be found for which both the kinetic energy operator and the potential energy  $E_g(Q_K)$  can be simultaneously written in the diagonal forms, *i.e.*,

$$-\frac{\hbar^2}{2} \sum_K \frac{1}{\mu_K} \frac{\partial^2}{\partial Q_K^2}$$

and

$$E_g^0 + \frac{1}{2} \sum_K Q_K^2 f_K )$$

Making this assumption for the moment, the Schrödinger equation for the vibrational states  $|\chi_n(Q_K)\rangle$  of the ground electronic state is that of a collection of 3P-6 independent harmonic oscillators,

$$\left[ \sum_K \left( -\frac{\hbar^2}{2\mu_K} \frac{\partial^2}{\partial Q_K^2} + \frac{1}{2} f_K Q_K^2 \right) + E_g^0 \right] |\chi_n\rangle = E_{g,n}^0 |\chi_n\rangle$$

(Here we have ignored the rotational and translation motion.)

The oscillators are independent because of the diagonal form. We have already solved the harmonic oscillator problem; the states  $|\chi_{\vec{v}}\rangle$  are products of 3N-6 Hermite polynomial states with energies

$$E_{g\vec{v}} = E_g^0 + \sum_K \left( v_K + \frac{1}{2} \right) \hbar \Omega_K,$$

where

$$\Omega_K = \sqrt{\frac{f_K}{\mu_K}}.$$

These eigenstates are analogous to the number states of the field oscillator, but there are only 3N-6 modes. The vector  $\vec{v}$  represents 3P-6 integers, giving the excitation level of each vibration,

$$|v_K \dots\rangle = |\chi(Q_K)\rangle = |v_1, \dots, v_K, \dots, v_{3P-6}\rangle = |v_1\rangle |v_2\rangle \dots |v_K\rangle \dots |v_{3P-6}\rangle$$

That is, the multimode vibrational state is simply a product of the Hermite polynomial states for each of the 3P-6 oscillators. Although these states are only eigenstates of the ground electronic state, they form a basis for (span the space of) the nuclear coordinates. Thus, we will take states of the form,

$$|\psi\rangle = |l_v\rangle |\vec{v}\rangle$$

as our 0<sup>th</sup> order states.

#### 4.6 Vibronic Coupling and the Approximate Vibronic States

Linear combinations of these 0<sup>th</sup> order states will approximately satisfy the full Schrödinger equation,

$$H = H_0 + H',$$

where  $H_0$  has the form,

$$H_0 = \left[ -\frac{\hbar^2}{2m_e} \sum_{i=1} \nabla_i^2 - \sum_p \sum_i \frac{Z_p e^2}{r_{o_{pi}}} + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{p>q} \frac{Z_p Z_q e^2}{R_{o_{pq}}} \right] + \left[ \frac{1}{2} \sum_K Q_K^2 f_K - \frac{\hbar^2}{2} \sum_K \frac{1}{\mu_K} \frac{\partial^2}{\partial Q_K^2} \right]$$

where the first bracket represents the 0<sup>th</sup> order *electronic* Hamiltonian and the second term is the 0<sup>th</sup> order *vibrational* Hamiltonian. The interaction Hamiltonian  $H'$  is just

$H' = H - H_0$ , where

$$H = \left[ -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_p \sum_i \frac{Z_p e^2}{r_{o_{pi}}} + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{p>q} \frac{Z_p Z_q e^2}{R_{o_{pq}}} \right] + \left[ \sum_K Q_K \left( \frac{\partial H}{\partial Q_K} \right)_0 + \frac{1}{2} \sum_{K,L} Q_K Q_L \left( \frac{\partial H}{\partial Q_K \partial Q_L} \right)_0 - \frac{\hbar^2}{2} \sum_K \frac{1}{\mu_K} \frac{\partial^2}{\partial Q_K^2} \right]$$

thus,

$$H' = \sum_K Q_K \left( \frac{\partial H}{\partial Q_K} \right)_0 + \frac{1}{2} \sum_{K,L} \left[ Q_K Q_L \left( \frac{\partial H}{\partial Q_K \partial Q_L} \right)_0 - f_K \delta_{K,L} \right].$$

$H'$  is the interaction that couples the 0<sup>th</sup> order electronic states with the 0<sup>th</sup> order vibrational states. We can now use this interaction Hamiltonian to obtain a perturbative solution to the vibronic coupling problem.

From time-dependent perturbation theory, the eigenstates to first order in the interaction,  $H'$ , are as shown below:

$$|l\rangle = |l\rangle_0 + \sum_{j \neq l} \frac{\langle j | \sum_K Q_K \left( \frac{\partial H'}{\partial Q_K} \right)_0 | l \rangle}{E_j^0 - E_l^0} |j\rangle_0 \left( 1 - e^{i(E_j^0 - E_l^0)(t_0 - t'_0)/\hbar} \right)$$

$$\begin{aligned}
& + \sum_j^0 \frac{\left\langle j \left| \sum_K \sum_L Q_K Q_L \left( \frac{\partial H'}{\partial Q_K \partial Q_L} \right)_0 - f_K \delta_{K,L} \right| l \right\rangle_0}{E_j^0 - E_l^0} |j\rangle_0 \left( 1 - e^{i(E_j^0 - E_l^0)(t_0 - t'_0)/\hbar} \right) + \dots \\
|l\rangle = & |l\rangle_0 + \sum_{j \neq l} \sum_K^0 \frac{\left\langle j \left| Q_K \left( \frac{\partial H'}{\partial Q_K} \right)_0 \right| l \right\rangle_0}{E_j^0 - E_l^0} |j\rangle_0 \left( 1 - e^{i(E_j^0 - E_l^0)(t_0 - t'_0)/\hbar} \right) \\
& + \sum_{j \neq l} \sum_{K,L}^0 \frac{\left\langle j \left| Q_K Q_L \left( \frac{\partial^2 H'}{\partial Q_K \partial Q_L} \right)_0 - f_K \delta_{K,L} \right| l \right\rangle_0}{E_j^0 - E_l^0} |j\rangle_0 \left( 1 - e^{i(E_j^0 - E_l^0)(t_0 - t'_0)/\hbar} \right) + \dots
\end{aligned}$$

Here, the 0<sup>th</sup> order states  $|l\rangle_0$  are just the product of a 0<sup>th</sup> order electronic states  $|l_v\rangle$  and a 0<sup>th</sup> order vibrational states  $|\vec{v}\rangle$ , *i.e.*,

$$|l\rangle_0 = |l_v\rangle |\vec{v}\rangle.$$

Substituting this for  $|l\rangle_0$ , we obtain the perturbative solutions to the full molecular Hamiltonian to first order. Notice that the first order states involve the energies only to 0<sup>th</sup> order.

$$\begin{aligned}
|l\rangle = & |l_v\rangle |\vec{v}\rangle - \sum_{j,\alpha} \sum_{\vec{u}} \sum_{K=1}^{3N-6} \frac{\langle j_\alpha | \left\langle \vec{u} \left| Q_K \left( \frac{\partial H'}{\partial Q_K} \right)_0 \right| \vec{v} \right\rangle |l_v\rangle |\vec{u}\rangle |j_\alpha\rangle}{E_{l_v\vec{v}} - E_{j_\alpha\vec{u}}} f_{j_\alpha\vec{u},l_v\vec{v}}(t_0) \\
& - \sum_{j,\alpha} \sum_{\vec{u}} \sum_{K,L=1}^{3N-6} \frac{\langle j_\alpha | \left\langle \vec{u} \left| \left( \frac{\partial^2 H'}{\partial Q_K \partial Q_L} \right)_0 Q_K Q_L \right| \vec{v} \right\rangle |l_v\rangle}{E_{l_v\vec{v}} - E_{j_\alpha\vec{u}}} |j_\alpha\rangle |\vec{u}\rangle f_{j_\alpha\vec{u},l_v\vec{v}}(t_0) + \dots \\
|l\rangle = & |l_v\rangle |\vec{v}\rangle - \sum_{j,\alpha} \sum_{\vec{u}} \sum_{K=1}^{3N-6} \frac{\langle j_\alpha | \left( \frac{\partial H'}{\partial Q_K} \right)_0 |l_v\rangle \langle \vec{u} | Q_K | \vec{v} \rangle}{E_{l_v\vec{v}} - E_{j_\alpha\vec{u}}} |j_\alpha\rangle |\vec{u}\rangle f_{j_\alpha\vec{u},l_v\vec{v}}(t_0) \\
& - \sum_{j,\alpha} \sum_{\vec{u}} \sum_{K,L=1}^{3N-6} \frac{\langle j_\alpha | \left( \frac{\partial^2 H'}{\partial Q_K \partial Q_L} \right)_0 |l_v\rangle \langle \vec{u} | Q_K Q_L | \vec{v} \rangle}{E_{l_v\vec{v}} - E_{j_\alpha\vec{u}}} |j_\alpha\rangle |\vec{u}\rangle f_{j_\alpha\vec{u},l_v\vec{v}}(t_0) \\
& + \text{high order perturbation terms and high order Taylor series expansion terms.}
\end{aligned}$$

The molecular states  $|l\rangle$  are the approximate vibro-electronic or vibronic states that we will use to introduce vibrational structure into our equations for the different types of spectra.

In the above we have used a result from perturbation theory. The state  $|i(t_0)\rangle$  of the molecule at time  $t_0$  after the vibrational-electronic interaction  $H'$  is turned on at  $t'_0$  is obtained from the coefficients

$$\langle f|i(t)\rangle = \langle f|U|i\rangle = U_{fi}.$$

This is the amplitude for the probability of starting in an initial 0<sup>th</sup> order eigenstate  $i$  and evolving to a 0<sup>th</sup> order eigenstate  $f$  in time  $t'_0$  to  $t_0$ , at which time the interaction with the field is turned on. The 0<sup>th</sup> order state  $i$  evolves according to

$$|i(t)\rangle = \sum_j |j\rangle \langle j|i(t)\rangle = \sum_j |j\rangle \langle j|U|i\rangle = \sum_j U_{ji} |j\rangle.$$

Now from our earlier result, to first order

$$U_{ji} = \delta_{ji} + \frac{\langle j|H'|i\rangle}{E_j - E_i} \left(1 - e^{i(E_j - E_i)(t_0 - t'_0)/\hbar}\right);$$

therefore, to first order the state at time  $t_0$  is

$$\begin{aligned} |l(t_0)\rangle &= \sum_j U_{jl} |j\rangle = \sum_j \left[ \delta_{jl} + \langle j|H'|l\rangle \frac{\left(1 - e^{i(E_j - E_l)(t_0 - t'_0)/\hbar}\right)}{E_j - E_l} \right] |j\rangle \\ &= |l\rangle + \sum_j \langle j|H'|l\rangle \frac{\left(1 - e^{i(E_j - E_l)(t_0 - t'_0)/\hbar}\right)}{E_j - E_l} |j\rangle. \end{aligned}$$

Substituting for the vibronic Hamiltonian leads to the improved molecular eigenstates given above.

Our next step is to evaluate the vibrational matrix elements in the above expression for the approximate vibronic states. The vibrational matrix elements can be evaluated by remembering that for a harmonic oscillator the coordinate can be expressed in terms of the creation and annihilation operator as

$$Q_k = \frac{1}{\sqrt{2}f_k} (A_k + A_k^\dagger)$$

Thus,

$$\begin{aligned}
 \langle \bar{u} | Q_K | \bar{v} \rangle &= \langle u_1, \dots, u_{3P-6} | Q_K | v_1, \dots, v_{3P-6} \rangle = \frac{1}{\sqrt{2f_K}} \langle u_1 | \dots \langle u_{3P-6} | (A_K + A_K^\dagger) | v_{3P-6} \rangle \dots | v_1 \rangle \\
 &= \frac{1}{\sqrt{2f_K}} \langle u_K | (A_K + A_K^\dagger) | v_K \rangle \langle u_1 | v_1 \rangle \dots \langle u_{3P-6} | v_{3P-6} \rangle \\
 &= \frac{1}{\sqrt{2f_K}} (\langle u_K | A_K | v_K \rangle + \langle u_K | A_K^\dagger | v_K \rangle) \\
 \langle \bar{u} | Q_K | \bar{v} \rangle &= \begin{cases} \frac{1}{\sqrt{2f_K}} \langle v_K - 1 | A_K | v_K \rangle, & \text{if } u_K = v_K - 1 \\ \frac{1}{\sqrt{2f_K}} \langle v_K + 1 | A_K^\dagger | v_K \rangle, & \text{if } u_K = v_K + 1 \end{cases}
 \end{aligned}$$

and all other  $u_L = v_L$  for  $L \neq K$ . Now, using the relationships that we proved earlier

$$A_K | v_K \rangle = (v_K \hbar \Omega_K)^{1/2} | v_K - 1 \rangle$$

and

$$A_K^\dagger | v_K \rangle = [(v_K + 1) \hbar \Omega_K]^{1/2} | v_K + 1 \rangle,$$

we have

$$\langle \bar{u} | Q_K | \bar{v} \rangle = \begin{cases} \frac{1}{\sqrt{2f_K}} [v_K \hbar \Omega_K]^{1/2}, & u_K = v_K - 1 \text{ and } u_L = v_L, \forall L \neq K \\ \frac{1}{\sqrt{2f_K}} [(v_K + 1) \hbar \Omega_K]^{1/2}, & u_K = v_K + 1 \text{ and } u_L = v_L, \forall L \neq K \\ 0, & \text{otherwise.} \end{cases}$$

The energies  $E_{l,\bar{v}}$  are the electronic energies  $E_{l_v}^0$  plus the vibrational energies,  $E_{\bar{v}}$ , the 0<sup>th</sup> order vibrational energies of the molecular states, given by

$$E_{\vec{v}} = \sum_{K=1}^{3P-6} \left( v_K + \frac{1}{2} \right) \hbar \Omega_K.$$

Thus, the 0<sup>th</sup> order molecular states have energies given by

$$E_{i,\vec{v}} = E_{i,v}^0 + \sum_{K=1}^{3P-6} \left( v_K + \frac{1}{2} \right) \hbar \Omega_K.$$

Similarly,

$$\langle \bar{u} | Q_K Q_L | \vec{v} \rangle = \langle \bar{u} | (A_K + A_K^\dagger)(A_L + A_L^\dagger) | \vec{v} \rangle = \langle \bar{u} | A_K A_L^\dagger | \vec{v} \rangle + \langle \bar{u} | A_K^\dagger A_L | \vec{v} \rangle + \langle \bar{u} | A_K A_L | \vec{v} \rangle + \langle \bar{u} | A_K^\dagger A_L^\dagger | \vec{v} \rangle,$$

and the matrix elements that survive are

$$\langle \bar{u} | Q_K Q_L | \vec{v} \rangle = \frac{1}{\sqrt{2f_K f_L}} \times \begin{cases} \langle v_K - 1, v_L + 1 | A_K A_L^\dagger | v_K, v_L \rangle \\ \langle v_K + 1, v_L - 1 | A_K^\dagger A_L | v_K, v_L \rangle \\ \langle v_K - 1, v_L - 1 | A_K A_L | v_K, v_L \rangle \\ \langle v_K + 1, v_L + 1 | A_K^\dagger A_L^\dagger | v_K, v_L \rangle \end{cases}$$

Evaluation of the matrix elements gives,

$$\langle \bar{u} | Q_K Q_L | \vec{v} \rangle = \begin{cases} \frac{\hbar}{2} \left[ \frac{v_K (v_L + 1)}{\mu_K \Omega_K \mu_L \Omega_L} \right]^{1/2}, & u_K = v_K - 1, u_L = v_L + 1, u_M = v_M, \forall M \neq K \\ \frac{\hbar}{2} \left[ \frac{(v_K + 1) v_L}{\mu_K \Omega_K \mu_L \Omega_L} \right]^{1/2}, & u_K = v_K + 1, u_L = v_L - 1, u_M = v_M, \forall M \neq K \\ \frac{\hbar}{2} \left[ \frac{v_K v_L}{\mu_K \Omega_K \mu_L \Omega_L} \right]^{1/2}, & u_K = v_K - 1, u_L = v_L - 1, u_M = v_M, \forall M \neq K \\ \frac{\hbar}{2} \left[ \frac{(v_K + 1)(v_L + 1)}{\mu_K \Omega_K \mu_L \Omega_L} \right]^{1/2}, & u_K = v_K + 1, u_L = v_L + 1, u_M = v_M, \forall M \neq K \end{cases}$$

$$= \frac{\hbar}{2\sqrt{\mu_K \Omega_K \mu_L \Omega_L}} \begin{cases} \sqrt{v_K (v_L + 1)}, & u_K = v_K - 1, u_L = v_L + 1 \\ \sqrt{(v_K + 1) v_L}, & u_K = v_K + 1, u_L = v_L - 1 \\ \sqrt{v_K v_L}, & u_K = v_K - 1, u_L = v_L - 1 \\ \sqrt{(v_K + 1)(v_L + 1)}, & u_K = v_K + 1, u_L = v_L + 1, \end{cases}$$

and for  $K = L$  this reduces to

$$\langle \vec{u} | Q_K^2 | \vec{v} \rangle = \frac{\hbar}{2\mu_K \Omega_K} \begin{cases} \sqrt{v_K(v_K+1)}, & u_K = v_K \\ v_K, & u_K = v_K - 2 \\ (v_K + 1), & u_K = v_K + 2. \end{cases} \quad (\text{Is this correct?})$$

In the next chapter, we use the approximate vibronic molecular states and these matrix elements to evaluate the expressions for different types of molecular spectra.