Appendix B. The Born-Oppenheimer Approximation

The Hamiltonian for a polyatomic molecule is

$$H(\vec{R},\vec{r}) = H_{nuc}(\vec{R}) + H_{el}(\vec{r};\vec{R}) \tag{1}$$

where $\vec{R}$ designates, collectively, the coordinates of all the nuclei and $\vec{r}$ denotes, collectively, the coordinates of all the electrons. We have (in atomic units)

$$H_{nuc}(\vec{R}) = \frac{-1}{2}\sum_i \frac{\nabla_i^{\,2}}{M_i} + \sum_{\substack{i,i'\\ i'>i}} \frac{Z_i Z_{i'}}{R_{ii'}} \tag{2}$$

where the index i runs over all the nuclei, M_i is the mass of the i^{th} nucleus, and $R_{i\,i'}$ is the distance between nuclei i and i'. The electronic Hamiltonian is

$$H_{el}(\vec{r};\vec{R}) = \frac{-1}{2}\sum_j \nabla_j^{\,2} - \sum_{\substack{i,j\\ i}} \frac{Z_i}{r_{ij}} + \sum_{\substack{j,j'\\ j'>j}} \frac{1}{r_{jj'}} \tag{3}$$

here the index j runs over all the electrons and $r_{i\,j}$ is the distance between nucleus i and electron j.

For each given set of nuclear coordinates $\vec{R}$, we can, in principal, solve for a complete set of electronic states

$$H_{el}(\vec{r};\vec{R})\phi_{el}^{(k)}(\vec{r};\vec{R}) = E_{el}^{(k)}(\vec{R})\phi_{el}^{(k)}(\vec{r};\vec{R}) \tag{4}$$

We can then expand the full wavefunction (nuclei plus electrons) in terms of this complete set of states, as follows

$$\Psi(\vec{r};\vec{R}) = \sum_k C_k(\vec{R})\phi_{el}^{(k)}(\vec{r};\vec{R}) \tag{5}$$

The expansion coefficient depend on $\vec{R}$. With expansion (5) the full Schroedinger equation becomes

$$H(\vec{r};\vec{R})\Psi(\vec{r};\vec{R})=\left[\,H_{nuc}(\vec{R})+H_{el}(\vec{r};\vec{R})\,\right]\Psi(\vec{r};\vec{R})=E\,\Psi(\vec{r};\vec{R}) \tag{6}$$

which E is the total energy (electrons plus nuclei).

If you insert Eq. (5) into Eq. (6), and then premultiply by $\phi_{el}^{(l)}(\vec{r};\vec{R})$ and integrate over $\vec{r}$, you can show, knowing that the $\phi_{el}^{(k)}(\vec{r};\vec{R})$ are orthogonal and normalized, that you obtain

$$\left[\sum_{\substack{i,i'\\ i'>i}}\frac{Z_iZ_{i'}}{R_{i\,i'}}+E_{el}^{(l)}\right]C_l(\vec{R})+\sum_k\left\langle \phi_{el}^{(l)}(\vec{r};\vec{R})\left|\frac{-1}{2}\sum_i\frac{\nabla_i^{\,2}}{M_i}\right|C_k(\vec{R})\phi_{el}^{(k)}(\vec{r};\vec{R})\right\rangle=E\,C_l(\vec{R}) \tag{7}$$

where the angle brackets denote integration over all the electronic coordinates. This is a set of coupled 2^{nd} order differential equations in the expansion coefficients C_l.

If we neglect any off-diagonal couplings (retain just the $k = l$ term in the summation), we obtain

$$\left[\sum_{\substack{i,i'\\ i'>i}}\frac{Z_iZ_{i'}}{R_{i\,i'}}+E_{el}^{(l)}\right]C_l(\vec{R})+\left\langle \phi_{el}^{(l)}(\vec{r};\vec{R})\left|\frac{-1}{2}\sum_i\frac{\nabla_i^{\,2}}{M_i}\right|C_l(\vec{R})\phi_{el}^{(l)}(\vec{r};\vec{R})\right\rangle=E\,C_l(\vec{R}) \tag{8}$$

The integral in angle brackets can be broken up schematically as follows

$$\left\langle \phi_{el}^{(l)}(\vec{r};\vec{R}) \middle| \frac{-1}{2}\sum_i \frac{\nabla_i^{\,2}}{M_i} \middle| C_l(\vec{R})\phi_{el}^{(l)}(\vec{r};\vec{R}) \right\rangle =$$

$$\left\langle \phi_{el}^{(l)}(\vec{r};\vec{R}) \middle| \ \phi_{el}^{(l)}(\vec{r};\vec{R}) \right\rangle \frac{-1}{2}\sum_i \frac{\nabla_i^{\,2}}{M_i} C_l(\vec{R}) -$$

$$\sum_i \frac{1}{M_i} \left\langle \phi_{el}^{(l)}(\vec{r};\vec{R}) \middle| \nabla_i \phi_{el}^{(l)}(\vec{r};\vec{R}) \right\rangle \cdot \nabla_i C_l(\vec{R}) + \tag{9}$$

$$\left\langle \phi_{el}^{(l)}(\vec{r};\vec{R}) \middle| \frac{-1}{2}\sum_i \frac{\nabla_i^{\,2}}{M_i} \middle| \phi_{el}^{(l)}(\vec{r};\vec{R}) \right\rangle C_l(\vec{R})$$

The first angle bracket on the right-hand-side can be eliminated because the $\phi_{el}^{(l)}(\vec{r};\vec{R})$ functions are normalized, so that we obtain

$$\left\langle \phi_{el}^{(l)}(\vec{r};\vec{R}) \middle| \frac{-1}{2}\sum_i \frac{\nabla_i^{\,2}}{M_i} \middle| C_l(\vec{R})\phi_{el}^{(l)}(\vec{r};\vec{R}) \right\rangle = \frac{-1}{2}\sum_i \frac{\nabla_i^{\,2}}{M_i} C_l(\vec{R}) -$$

$$\sum_i \frac{1}{M_i} \left\langle \phi_{el}^{(l)}(\vec{r};\vec{R}) \middle| \nabla_i \phi_{el}^{(l)}(\vec{r};\vec{R}) \right\rangle \cdot \nabla_i C_l(\vec{R}) + \tag{10}$$

$$\left\langle \phi_{el}^{(l)}(\vec{r};\vec{R}) \middle| \frac{-1}{2}\sum_i \frac{\nabla_i^{\,2}}{M_i} \middle| \phi_{el}^{(l)}(\vec{r};\vec{R}) \right\rangle C_l(\vec{R})$$

If we neglect the second and third terms on the right-hand-side of Eq. (10), then we obtain the Born-Oppenheimer approximation, in which Eq. (8) becomes

$$\left[\frac{-1}{2}\sum_i \frac{\nabla_i^{\,2}}{M_i} + \sum_{\substack{i,i' \\ i'>i}} \frac{Z_i Z_{i'}}{R_{ii'}} + E_{el}^{(l)}(R) \right] C_l(\vec{R}) = E\, C_l(\vec{R}) \tag{11}$$

Thus the sum of the $\vec{R}$ dependent electronic energy and the nuclear repulsion energy provide the effective potential energy for the $C_l(\vec{R})$ functions, which describe the motion of the nuclei. The total wavefunction [Eq. (5)] becomes, in the B.O. approximation

$$\Psi_l(\vec{r};\vec{R}) = C_l(\vec{R})\phi_{el}^{(l)}(\vec{r};\vec{R}) \tag{12}$$

which is a product of a nuclear function times the electronic wavefunction.

In fact, Eq. (11) can be easily corrected by including the second derivative term from Eq. (11), as follows:

$$\left[\frac{-1}{2}\sum_i \frac{\nabla_i^2}{M_i} + \sum_{\substack{i,i' \\ i'>i}} \frac{Z_i Z_{i'}}{R_{ii'}} + E_{el}^{(l)}(R) + \left\langle \phi_{el}^{(l)}(\vec{r};\vec{R}) \middle| \frac{-1}{2}\sum_i \frac{\nabla_i^2}{M_i} \middle| \phi_{el}^{(l)}(\vec{r};\vec{R}) \right\rangle\right] C_l(\vec{R}) = E\, C_l(\vec{R}) \tag{13}$$