1 THE BORN–OPPENHEIMER APPROXIMATION

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The Born–Oppenheimer (BO) approximation is used in the solution of the rovibronic wave equation, and every chapter of this book implicitly or explicitly involves it; either the BO approximation is assumed or else its breakdown is specifically considered. Thus it is appropriate that the opening chapter explain briefly what this approximation is. Although not always appreciated there are two ways of making the BO approximation: the perturbation theory approach [Born and Oppenheimer (1927); see also Sections 14 and 15, and Appendix VII, of Born and Huang (1954), and Mead (1988)], and the variation theory approach [Born (1951); see also Appendix VII of Born and Huang (1954)]. Before outlining these two approaches we first write out the nonrelativistic rovibronic Hamiltonian in order to introduce the notation used [see, for example, Bunker and Jensen (1998) for the details of the derivation].

We consider a molecule as consisting of l particles, N of which are nuclei and $l - N$ of which are electrons. The derivation of the rovibronic Hamiltonian involves first separating off translation, and then (in order to facilitate the separation of nuclear and electronic motion) referring the coordinates of all particles in the molecule to a (ξ, η, ζ) axis system that has origin at the nuclear center of mass, but with arbitrary space-fixed orientation. Doing this the exact nonrelativistic

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(spin-free) rovibronic Hamiltonian is obtained as [see, for example, equations (9–48) of Bunker and Jensen (1998)]:

$$\hat{H}_{\rm rve} = \hat{T}_{\rm e}^{0} + \hat{T}_{\rm e}' + \hat{T}_{\rm N} + V(\boldsymbol{R}_{\rm N}, \boldsymbol{r}_{\rm elec}), \tag{1}$$

where

$$\hat{T}_{\rm e}^{0} = -\frac{\hbar^2}{2m_{\rm e}} \sum_{i=N+1}^{l} \nabla_i^2, \tag{2}$$

$$\hat{T}_{\rm e}' = -\frac{\hbar^2}{2M_{\rm N}} \sum_{i,j=N+1}^{l} \nabla_i \cdot \nabla_j, \tag{3}$$

$$\hat{T}_{\rm N} = -\frac{\hbar^2}{2} \sum_{i=2}^{N} \frac{\nabla_i^2}{m_i} + \frac{\hbar^2}{2M_{\rm N}} \sum_{i,j=2}^{N} \nabla_i \cdot \nabla_j, \tag{4}$$

$$\nabla_i^2 = \frac{\partial^2}{\partial \xi_i^2} + \frac{\partial^2}{\partial \eta_i^2} + \frac{\partial^2}{\partial \zeta_i^2}, \tag{5}$$

$$\nabla_i \cdot \nabla_j = \frac{\partial^2}{\partial \xi_i \partial \xi_j} + \frac{\partial^2}{\partial \eta_i \partial \eta_j} + \frac{\partial^2}{\partial \zeta_i \zeta_j}, \tag{6}$$

and

$$V(\boldsymbol{R}_{\rm N}, \boldsymbol{r}_{\rm elec}) = \sum_{r<s=1}^{l} \frac{C_r C_s e^2}{4\pi\varepsilon_0 R_{rs}}. \tag{7}$$

In these equations the mass of each nucleus is m_i, the total mass of all the nuclei is $M_{\rm N}$, the mass of the electron is $m_{\rm e}$, the charge of each particle is $C_r e$ ($C_r = -1$ for the electron), and R_{rs} is the separation of particles r and s. We explicitly show that the potential energy function V depends on the nuclear coordinates $\boldsymbol{R}_{\rm N} = (\xi_2, \eta_2, \zeta_2, \xi_3, \eta_3, \zeta_3, \ldots, \xi_N, \eta_N, \zeta_N)$ and on the electronic coordinates $\boldsymbol{r}_{\rm elec} = (\xi_{N-1}, \eta_{N+1}, \zeta_{N+1}, \xi_{N+2}, \eta_{N+2}, \zeta_{N+2}, \ldots, \xi_l, \eta_l, \zeta_l)$. In these (ξ, η, ζ) coordinates (with the origin at the nuclear center of mass) the kinetic energy is completely separable into an electronic part $\hat{T}_{\rm e} = \hat{T}_{\rm e}^{0} + \hat{T}_{\rm e}'$, and a nuclear part $\hat{T}_{\rm N}$. We now consider the two ways of making the BO approximation in order to solve the rovibronic wave equation

$$\left[\hat{H}_{\rm rve} - E_{{\rm rve},m}\right] \Psi_{{\rm rve},m}(\boldsymbol{r}_{\rm elec}, \boldsymbol{R}_{\rm N}) = 0. \tag{8}$$

1.1 The perturbation theory approach

Born and Oppenheimer (1927) (called BandO from here on) begin in their introduction with the fundamental idea that the rovibronic Hamiltonian should be expanded in powers of the parameter κ, where κ is given by the fourth root of the ratio of the mass of the electron to the mean nuclear mass M_0, i.e.,

$$\kappa = \left(\frac{m_{\rm e}}{M_{\rm N}/N}\right)^{1/4} = \left(\frac{m_{\rm e}}{M_0}\right)^{1/4}. \tag{9}$$

Born and Heisenberg (1924) had earlier suggested an expansion in $\sqrt{m_{\rm e}/M_0}$. Using their expansion parameter BandO show (as we see below) that, with the electronic energy appearing in zeroth order, the vibrational energy appears in second order, and the rotational energy in fourth order, while the first- and third-order terms disappear.

The second idea in BandO is that the vibrational displacement coordinates are κ times the size of the bond lengths or bond angles. This is expressed by writing

$$\boldsymbol{R}_{\mathrm{N}} = \boldsymbol{R}_{\mathrm{N}}^{0} + \kappa \boldsymbol{U}_{\mathrm{N}}, \tag{10}$$

from which it follows that

$$\frac{\partial}{\partial \boldsymbol{R}_{\mathrm{N}}} = \frac{1}{\kappa}\frac{\partial}{\partial \boldsymbol{U}_{\mathrm{N}}}. \tag{11}$$

In equation (10) $\boldsymbol{R}_{\mathrm{N}}^{0}$ is an as yet unspecified molecular reference configuration, and the rotational coordinates are contained in the $\boldsymbol{R}_{\mathrm{N}}^{0}$ coordinates. BandO show that this reference configuration has to be the equilibrium molecular configuration, and we will see why this is when we repeat their analysis of the first order result below.

The third important part of the development made by BandO, which follows after introducing the vibrational displacement coordinates $\boldsymbol{U}_{\mathrm{N}}$ in equation (10), is that the following order of magnitude relation holds:

$$\frac{\partial \Psi_{\mathrm{rve}}}{\partial \boldsymbol{r}_{\mathrm{elec}}} \sim \frac{\partial \Psi_{\mathrm{rve}}}{\partial \boldsymbol{U}_{\mathrm{N}}}. \tag{12}$$

This equation is necessary in order to relate the orders of magnitude of $\hat{T}_{\mathrm{N}}$ and $\hat{T}_{\mathrm{e}}^{0}$.

The treatment in BandO depends on the following two conditions:

- That the vibrational energy separations be two orders of magnitude smaller than the electronic energy separations, i.e.,

$$\Delta E_{\mathrm{vib}} \sim \kappa^{2}\, \Delta E_{\mathrm{elec}}, \tag{13}$$

and

- That the rotational energy separations be two orders of magnitude smaller than the vibrational energy separations, i.e.,

$$\Delta E_{\mathrm{rot}} \sim \kappa^{2}\, \Delta E_{\mathrm{vib}}. \tag{14}$$

When these conditions are in accord with the experimental observations the BO approximation as treated in BandO will be valid.

To begin the perturbation theory treatment the rovibronic Hamiltonian is written as

$$\hat{H}_{\mathrm{rve}} = \hat{H}_{0} + \hat{T}_{\mathrm{e}}' + \hat{T}_{\mathrm{N}}, \tag{15}$$

where the electronic Hamiltonian is defined as

$$\hat{H}_{0} = \hat{T}_{\mathrm{e}}^{0} + V\left(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}}\right). \tag{16}$$

The electronic wave equation

$$\left[\hat{H}_{0} - E_{\mathrm{elec},n}\right] \Phi_{\mathrm{elec},n}(\boldsymbol{r}_{\mathrm{elec}}; \boldsymbol{R}_{\mathrm{N}}) = 0, \tag{17}$$

is supposed solved, with the $\boldsymbol{r}_{\mathrm{elec}}$ as dynamical variables and n as the electronic state quantum number, for $\boldsymbol{R}_{\mathrm{N}} = \boldsymbol{R}_{\mathrm{N}}^{0}$ and for neighbouring molecular configurations around $\boldsymbol{R}_{\mathrm{N}}^{0}$. In the approach of BandO the nth solution of the electronic wave equation is obtained by a perturbation theory expansion about the solution at $\boldsymbol{R}_{\mathrm{N}} = \boldsymbol{R}_{\mathrm{N}}^{0}$ using equation (10) to give:

$$\hat{H}_{0} = \hat{H}_{0}^{(0)} + \kappa \hat{H}_{0}^{(1)} + \kappa^{2} \hat{H}_{0}^{(2)} + \ldots, \tag{18}$$

$$\Phi_{\mathrm{elec},n} = \Phi_{\mathrm{elec},n}^{(0)} + \kappa \Phi_{\mathrm{elec},n}^{(1)} + \kappa^{2} \Phi_{\mathrm{elec},n}^{(2)} + \ldots, \tag{19}$$

and

$$E_{\mathrm{elec},n} = E^{(0)}_{\mathrm{elec},n} + \kappa E^{(1)}_{\mathrm{elec},n} + \kappa^2 E^{(2)}_{\mathrm{elec},n} + \dots, \tag{20}$$

where $\hat{H}_0^{(0)}$, $\Phi^{(0)}_{\mathrm{elec},n}$ and $E^{(0)}_{\mathrm{elec},n}$ are independent of U_N (being appropriate for $\boldsymbol{R}_\mathrm{N} = \boldsymbol{R}^0_\mathrm{N}$). $\hat{H}_0^{(r)}$ is an operator with respect to the coordinates $\boldsymbol{r}_\mathrm{elec}$ and, along with $\Phi^{(r)}_{\mathrm{elec},n}$ and $E^{(r)}_{\mathrm{elec},n}$, it is a homogeneous function of degree r in the U_N. In the notation of BandO equations (18)–(20) above are given in their equations (16)–(18), where they use the notation ξ, ζ and V_n for what we call $\boldsymbol{R}_\mathrm{N}$, $\boldsymbol{U}_\mathrm{N}$ and $E_{\mathrm{elec},n}$. Substituting equations (18)–(20) into equation (17) and equating like powers of κ we obtain:

$$\left[\hat{H}_0^{(0)} - E^{(0)}_{\mathrm{elec},n}\right] \Phi^{(0)}_{\mathrm{elec},n} = 0. \tag{21}$$

$$\left[\hat{H}_0^{(0)} - E^{(0)}_{\mathrm{elec},n}\right] \Phi^{(1)}_{\mathrm{elec},n} = -\left[\hat{H}_0^{(1)} - E^{(1)}_{\mathrm{elec},n}\right] \Phi^{(0)}_{\mathrm{elec},n}. \tag{22}$$

$$\left[\hat{H}_0^{(0)} - E^{(0)}_{\mathrm{elec},n}\right] \Phi^{(2)}_{\mathrm{elec},n} = -\left[\hat{H}_0^{(1)} - E^{(1)}_{\mathrm{elec},n}\right] \Phi^{(1)}_{\mathrm{elec},n} - \left[\hat{H}_0^{(2)} - E^{(2)}_{\mathrm{elec},n}\right] \Phi^{(0)}_{\mathrm{elec},n}. \tag{23}$$

etc., where equation (21) is obtained from the κ^0 coefficients, equation (22) is obtained from the κ^1 coefficients, and equation (23) is obtained from the κ^2 coefficients.

To make an order of magnitude expansion of the complete Hamiltonian $\hat{H}_\mathrm{rve}$ we have to determine the orders of magnitude of $\hat{T}'_\mathrm{e}$ and $\hat{T}_\mathrm{N}$ given in equations (3) and (4) respectively. Comparing the mass coefficient of $\hat{T}'_\mathrm{e}$ with that of $\hat{T}^0_\mathrm{e}$ it is obvious that $\hat{T}'_\mathrm{e}$ is of order of magnitude $\kappa^4 \hat{H}_0$, and so we can express its order of magnitude by writing

$$\hat{T}'_\mathrm{e} = \kappa^4 \hat{H}_1^{(0)}. \tag{24}$$

To determine the order of magnitude of $\hat{T}_\mathrm{N}$ we have to consider both the size of its mass coefficient and the size of the derivative $\partial^2 \Psi_\mathrm{rve} / \partial \boldsymbol{R}_\mathrm{N}{}^2$. Using equation (11) for the vibrational part of $\hat{T}_\mathrm{N}$ [called $\hat{T}_\mathrm{N}(\mathrm{vib})$], which is expressed solely in terms of derivatives of degree two with respect to the displacement coordinates, it follows that

$$\hat{T}_\mathrm{N}(\mathrm{vib}) = \hat{T}_\mathrm{N}\left(\frac{\partial^2}{\partial \boldsymbol{R}^2_\mathrm{N}}\right) \sim \frac{1}{\kappa^2} \hat{T}_\mathrm{N}\left(\frac{\partial^2}{\partial \boldsymbol{U}^2_\mathrm{N}}\right). \tag{25}$$

Using equation (12), together with a consideration of the sizes of the mass coefficients, there is the order of magnitude relation:

$$\hat{T}_\mathrm{N}\left(\frac{\partial^2}{\partial \boldsymbol{U}^2_\mathrm{N}}\right) \sim \kappa^4 \hat{H}_0. \tag{26}$$

Substituting equation (26) into equation (25) we obtain the required order of magnitude estimate.

$$\hat{T}_\mathrm{N}(\mathrm{vib}) \sim \kappa^2 \hat{H}_0. \tag{27}$$

The order of magnitude of the rotational part of $\hat{T}_\mathrm{N}$ (which contains no derivatives with respect to the displacement coordinates) is $\kappa^4 H_0$, and the order of magnitude of the rotational–vibration coupling part of $\hat{T}_\mathrm{N}$ (which contains derivatives of degree one with respect to the displacement coordinates) is $\kappa^3 \hat{H}_0$. To express these orders of magnitude we write

$$\begin{aligned}\hat{T}_\mathrm{N} &= \kappa^2 \hat{H}_{2\mathrm{v}} + \kappa^3 \hat{H}_{2\mathrm{rv}} + \kappa^4 \hat{H}_{2\mathrm{r}} \\ &= \kappa^2 \hat{H}^{(0)}_{2\mathrm{v}} + \kappa^3\left(\hat{H}^{(0)}_{2\mathrm{rv}} + \hat{H}^{(1)}_{2\mathrm{v}}\right) + \kappa^4\left(\hat{H}^{(0)}_{2\mathrm{r}} + \hat{H}^{(1)}_{2\mathrm{rv}} + \hat{H}^{(2)}_{2\mathrm{v}}\right).\end{aligned} \tag{28}$$

This is given in equation (29) of BandO, and the above order of magnitude breakdown of the factors $\hat{H}_{2v}$, $\hat{H}_{2rv}$, and $\hat{H}_{2r}$ is copied from them. Note that $\hat{H}_{2v}^{(0)}$ involves quadratic derivatives with respect to the vibrational displacement coordinates. Thus to fourth order the rovibronic Hamiltonian written as an order of magnitude expansion is

$$\hat{H}_{\mathrm{rve}} = \hat{H}_0^{(0)} + \kappa\hat{H}_0^{(1)} + \kappa^2\left(\hat{H}_0^{(2)} + \hat{H}_{2v}^{(0)}\right) + \kappa^3\left(\hat{H}_0^{(3)} + \hat{H}_{2rv}^{(0)} + \hat{H}_{2v}^{(1)}\right) + \kappa^4\left(\hat{H}_0^{(4)} + \hat{H}_1^{(0)} + \hat{H}_{2r}^{(0)} + \hat{H}_{2rv}^{(1)} + \hat{H}_{2v}^{(2)}\right). \tag{29}$$

To implement perturbation theory for solving the rovibronic wave equation [equation (8)] we expand the eigenfunctions and eigenvalues of $\hat{H}_{\mathrm{rve}}$ as

$$\Psi_{\mathrm{rve},m} = \Psi_{\mathrm{rve},m}^{(0)} + \kappa\Psi_{\mathrm{rve},m}^{(1)} + \kappa^2\Psi_{\mathrm{rve},m}^{(2)} + \ldots, \tag{30}$$

and

$$E_{\mathrm{rve},m} = E_{\mathrm{rve},m}^{(0)} + \kappa E_{\mathrm{rve},m}^{(1)} + \kappa^2 E_{\mathrm{rve},m}^{(2)} + \ldots. \tag{31}$$

As in the perturbation theory treatment of the electronic wave equation in equations (21)–(23) above, we now substitute equations (29)–(31) into equation (8), and equate like powers of κ. If we stop at second order we obtain:

$$\left[\hat{H}_0^{(0)} - E_{\mathrm{rve},m}^{(0)}\right]\Psi_{\mathrm{rve},m}^{(0)} = 0, \tag{32}$$

$$\left[\hat{H}_0^{(0)} - E_{\mathrm{rve},m}^{(0)}\right]\Psi_{\mathrm{rve},m}^{(1)} = -\left[\hat{H}_0^{(1)} - E_{\mathrm{rve},m}^{(1)}\right]\Psi_{\mathrm{rve},m}^{(0)}, \tag{33}$$

and

$$\left[\hat{H}_0^{(0)} - E_{\mathrm{rve},m}^{(0)}\right]\Psi_{\mathrm{rve},m}^{(2)} = -\left[\hat{H}_0^{(1)} - E_{\mathrm{rve},m}^{(1)}\right]\Psi_{\mathrm{rve},m}^{(1)} - \left[\hat{H}_0^{(2)} + \hat{H}_{2v}^{(0)} - E_{\mathrm{rve},m}^{(2)}\right]\Psi_{\mathrm{rve},m}^{(0)}. \tag{34}$$

In zero order, comparing equations (21) and (32), we deduce that

$$E_{\mathrm{rve},m}^{(0)} = E_{\mathrm{elec},n}^{(0)}, \tag{35}$$

and that $\Phi_{\mathrm{elec},n}^{(0)} = \Phi_{\mathrm{elec},n}(\boldsymbol{r}_{\mathrm{elec}};\boldsymbol{R}_{\mathrm{N}}^0)$ is a solution of the zero-order rovibronic equation (32). The product of this electronic function with an arbitrary function of $\boldsymbol{U}_{\mathrm{N}}$, $\Phi_{\mathrm{nuc}}^{(0)}(\boldsymbol{U}_{\mathrm{N}})$ say, will also be a solution, and thus, in general:

$$\Psi_{\mathrm{rve},m}^{(0)}(\boldsymbol{r}_{\mathrm{elec}},\boldsymbol{U}_{\mathrm{N}}) = \Phi_{\mathrm{nuc}}^{(0)}(\boldsymbol{U}_{\mathrm{N}})\Phi_{\mathrm{elec},n}^{(0)}(\boldsymbol{r}_{\mathrm{elec}}) = \Phi_{\mathrm{nuc}}^{(0)}(\boldsymbol{U}_{\mathrm{N}})\Phi_{\mathrm{elec},n}\left(\boldsymbol{r}_{\mathrm{elec}};\boldsymbol{R}_{\mathrm{N}}^0\right). \tag{36}$$

The arbitrariness in the function $\Phi_{\mathrm{nuc}}^{(0)}(\boldsymbol{U}_{\mathrm{N}})$ disappears when we take the treatment to second order.

Multiplying the left hand side of equation (33) on the left by $\Phi_{\mathrm{elec},n}^{(0)*}$ and integrating over $\boldsymbol{r}_{\mathrm{elec}}$ gives zero from equations (21) and (35). Thus multiplying the right hand side on the left by $\Phi_{\mathrm{elec},n}^{(0)*}$ and integrating over $\boldsymbol{r}_{\mathrm{elec}}$ gives zero, so we have

$$\left\langle\Phi_{\mathrm{elec},n}^{(0)}\right|\left(\hat{H}_0^{(1)} - E_{\mathrm{rve},m}^{(1)}\right)\left|\Psi_{\mathrm{rve},m}^{(0)}\right\rangle = \Phi_{\mathrm{nuc}}^{(0)}(\boldsymbol{U}_{\mathrm{N}})\left\langle\Phi_{\mathrm{elec},n}^{(0)}\right|\left(\hat{H}_0^{(1)} - E_{\mathrm{rve},m}^{(1)}\right)\left|\Phi_{\mathrm{elec},n}^{(0)}\right\rangle = 0, \tag{37}$$

where we integrate only over $\boldsymbol{r}_{\mathrm{elec}}$. However, if we multiply equation (22) by $\Phi_{\mathrm{elec},n}^{(0)}$ and integrate over $\boldsymbol{r}_{\mathrm{elec}}$ we obtain

$$\left\langle\Phi_{\mathrm{elec},n}^{(0)}\right|\left(\hat{H}_0^{(0)} - E_{\mathrm{elec},n}^{(0)}\right)\left|\Phi_{\mathrm{elec},n}^{(1)}\right\rangle = -\left\langle\Phi_{\mathrm{elec},n}^{(0)}\right|\left(\hat{H}_0^{(1)} - E_{\mathrm{elec},n}^{(1)}\right)\left|\Phi_{\mathrm{elec},n}^{(0)}\right\rangle = 0, \tag{38}$$

from which we deduce, by comparing with equation (37), that we must have

$$E^{(1)}_{\mathrm{rve},m} = E^{(1)}_{\mathrm{elec},n}. \tag{39}$$

However $E^{(1)}_{\mathrm{rve},m}$, like $E_{\mathrm{rve},m}$, is a constant independent of U_{N}, whereas $E^{(1)}_{\mathrm{elec},n}$ is a linear function of U_{N}; this implies that we must have

$$E^{(1)}_{\mathrm{elec},n} = 0, \tag{40}$$

and the linear term in equation (20) vanishes. This means that $\partial E_{\mathrm{elec},n}/\partial U_{\mathrm{N}} = 0$, and thus the reference molecular configuration $\boldsymbol{R}^0_{\mathrm{N}}$ has to be the equilibrium molecular configuration for each electronic state n. Setting $E^{(1)}_{\mathrm{elec},n}$ and $E^{(1)}_{\mathrm{rve},m}$ equal to zero in equations (22) and (33), and comparing the two equations, we see that $\Phi^{(0)}_{\mathrm{nuc}}(U_{\mathrm{N}})\Phi^{(1)}_{\mathrm{elec},n}(\boldsymbol{r}_{\mathrm{elec}}; \boldsymbol{R}_{\mathrm{N}})$ is a solution of the inhomogeneous equation (33). It is still a solution if we add any solution of the corresponding homogeneous equation so that, in general, the first-order rovibronic wavefunction term is

$$\Psi^{(1)}_{\mathrm{rve},m}(\boldsymbol{r}_{\mathrm{elec}}; \boldsymbol{R}_{\mathrm{N}}) = \Phi^{(0)}_{\mathrm{nuc}}(U_{\mathrm{N}})\Phi^{(1)}_{\mathrm{elec},n}(\boldsymbol{r}_{\mathrm{elec}}; \boldsymbol{R}_{\mathrm{N}}) + \Phi^{(1)}_{\mathrm{nuc}}(U_{\mathrm{N}})\Phi^{(0)}_{\mathrm{elec},n}(\boldsymbol{r}_{\mathrm{elec}}), \tag{41}$$

where $\Phi^{(1)}_{\mathrm{nuc}}(U_{\mathrm{N}})$ is another, as yet, arbitrary function of U_{N}.

Using equations (36), (40) and (41), the second-order rovibronic equation (34) can be rewritten

$$\begin{aligned}\left[\hat{H}^{(0)}_{0} - E^{(0)}_{\mathrm{rve},m}\right]\Psi^{(2)}_{\mathrm{rve},m} = {}& -\hat{H}^{(1)}_{0}\left[\Phi^{(0)}_{\mathrm{nuc}}\Phi^{(1)}_{\mathrm{elec},n} + \Phi^{(1)}_{\mathrm{nuc}}\Phi^{(0)}_{\mathrm{elec},n}\right] \\ & - \left[\hat{H}^{(2)}_{0} + \hat{H}^{(0)}_{2\mathrm{v}} - E^{(2)}_{\mathrm{rve},m}\right]\Phi^{(0)}_{\mathrm{nuc}}\Phi^{(0)}_{\mathrm{elec},n}.\end{aligned} \tag{42}$$

If we subtract $\Phi^{(1)}_{\mathrm{nuc}}$ times equation (22) and $\Phi^{(0)}_{\mathrm{nuc}}$ times equation (23) from equation (42) we obtain

$$\begin{aligned}&\left[\hat{H}^{(0)}_{0} - E^{(0)}_{\mathrm{rve},m}\right]\left[\Psi^{(2)}_{\mathrm{rve},m} - \Phi^{(1)}_{\mathrm{nuc}}\Phi^{(1)}_{\mathrm{elec},n} - \Phi^{(0)}_{\mathrm{nuc}}\Phi^{(2)}_{\mathrm{elec},n}\right] \\ &\quad = -\left[\hat{H}^{(0)}_{2\mathrm{v}} + E^{(2)}_{\mathrm{elec},n} - E^{(2)}_{\mathrm{rve},m}\right]\Phi^{(0)}_{\mathrm{nuc}}\Phi^{(0)}_{\mathrm{elec},n}.\end{aligned} \tag{43}$$

The condition for the solution of this equation is that

$$\left\langle \Phi^{(0)}_{\mathrm{elec},n}\right|\left[\hat{H}^{(0)}_{2\mathrm{v}} + E^{(2)}_{\mathrm{elec},n} - E^{(2)}_{\mathrm{rve},m}\right]\left|\Phi^{(0)}_{\mathrm{nuc}}\Phi^{(0)}_{\mathrm{elec},n}\right\rangle = 0. \tag{44}$$

The integration in equation (44) is over $\boldsymbol{r}_{\mathrm{elec}}$ and $[\hat{H}^{(0)}_{2\mathrm{v}} + E^{(2)}_{\mathrm{elec},n} - E^{(2)}_{\mathrm{rve},m}]\Phi^{(0)}_{\mathrm{nuc}}$ is independent of $\boldsymbol{r}_{\mathrm{elec}}$. Therefore, the condition reduces to

$$\left[\hat{H}^{(0)}_{2\mathrm{v}} + E^{(2)}_{\mathrm{elec},n} - E^{(2)}_{\mathrm{rve},m}\right]\Phi^{(0)}_{\mathrm{nuc}} = 0. \tag{45}$$

Equation (45) determines the vibrational wavefunction $\Phi^{(0)}_{\mathrm{vib}} = \Phi^{(0)}_{\mathrm{nuc}}$ and the second-order correction to the vibronic energy.

It is instructive to stop here in the development and to ponder the result. If we multiply equation (45) by κ^2 then $\kappa^2\hat{H}^{(0)}_{2\mathrm{v}}$ is the vibrational kinetic energy of the nuclei, $\kappa^2 E^{(2)}_{\mathrm{elec},n}$ acts as a potential function for the nuclear vibrational motion (note that it is a quadratic function of U_{N}), and $\kappa^2 E^{(2)}_{\mathrm{rve},m}$ is the second-order correction to the vibronic energy that is derived. At this level of approximation the potential function for the nuclear motion is a quadratic function of the nuclear displacements U_{N}; as a result we will call this the *harmonic Born-Oppenheimer approximation*. In the harmonic BO approximation the vibronic wavefunction is determined only to zero order [from equation (36)] as the product of the vibrational wavefunction $\Phi^{(0)}_{\mathrm{nuc}}(\boldsymbol{U}_{\mathrm{N}})$ [from equation (45)] and the electronic wavefunction $\Phi_{\mathrm{elec},n}(\boldsymbol{r}_{\mathrm{elec}};\boldsymbol{R}^0_{\mathrm{N}})$. From equations (35), (31) and (45) we see that the vibronic eigenvalue is the sum of $E^{(0)}_{\mathrm{elec},n}$ (the electronic energy when the nuclei are at the equilibrium configuration) and $\kappa^2 E^{(2)}_{\mathrm{rve},m}$ where this second-order energy correction is obtained from the harmonic vibration wave equation equation (45). Anharmonicity, and the rotational energies, are of too small an order of magnitude to be considered in the harmonic BO approximation.

The perturbation treatment can be carried to higher order and the fourth-order result is important; this leads to the *quartic BO approximation*. To derive this one uses the expression for $\hat{H}_{\mathrm{rve}}$ given in equation (29). The algebra from BandO involved in the fourth-order development is also given in Appendix VII of Born and Huang (1954), and we summarize it. The rovibronic wavefunction obtained can be written as

$$\begin{aligned}\Psi_{\mathrm{rve},m}(\boldsymbol{r}_{\mathrm{elec}},\boldsymbol{U}_{\mathrm{N}}) &= \left[\Phi^{(0)}_{\mathrm{nuc}}(\boldsymbol{U}_{\mathrm{N}}) + \kappa\Phi^{(1)}_{\mathrm{nuc}}(\boldsymbol{U}_{\mathrm{N}}) + \kappa^2\Phi^{(2)}_{\mathrm{nuc}}(\boldsymbol{U}_{\mathrm{N}})\right]\Phi_{\mathrm{elec},n}(\boldsymbol{r}_{\mathrm{elec}};\boldsymbol{R}_{\mathrm{N}}) \\ &= \tilde{\Phi}_{\mathrm{rv}}(\boldsymbol{U}_{\mathrm{N}})\Phi_{\mathrm{elec},n}(\boldsymbol{r}_{\mathrm{elec}};\boldsymbol{R}_{\mathrm{N}}), \qquad (46)\end{aligned}$$

and the rovibronic energy is obtained by solving an equation like equation (45), but in which the potential function is developed to quartic powers of the nuclear displacement coordinates $\boldsymbol{U}_{\mathrm{N}}$ and the kinetic energy is the rotation–vibration kinetic energy operator $\kappa^2\hat{H}_{2\mathrm{v}} + \kappa^3\hat{H}_{2\mathrm{rv}} + \kappa^4\hat{H}_{2\mathrm{r}}$. The quartic potential function is termed an *effective* potential function since it involves the effect of the electronic kinetic energy term $\kappa^4\hat{H}^{(0)}_{1}$ [see equation (24)] as well as the effect of the vibrational kinetic energy term acting on the electronic wavefunction.

The important result is that in the (fourth-order) quartic BO approximation the rovibronic wavefunction is still obtained as the product of a rotation–vibration wavefunction $\tilde{\Phi}_{\mathrm{rv}}$, that depends only on $\boldsymbol{U}_{\mathrm{N}}$, and a single electronic wavefunction, obtained by solving the electronic wave equation at fixed nuclear coordinates. Since the electronic wavefunction is represented as a single function it does not involve coupling with other electronic states, and the quartic BO approximation maintains the adiabatic separation of the electronic from the rotation–vibration degrees of freedom.

Using perturbation theory for an isolated ground electronic state of a diatomic molecule Watson (1980) shows that the eigenvalues can be written as the standard *Dunham expansion* [Dunham (1932)]

$$E_{vJ} = hc\sum_{k=0}^{\infty}\sum_{l=0}^{\infty} Y_{kl}\left(v+\frac{1}{2}\right)^{k}\left[J(J+1)-\Lambda^2\right]^{l}, \qquad (47)$$

where v is the vibrational quantum number, J is the rotational quantum number, and Λ is the projection of the electronic angular momentum on the molecular axis in units of $\hbar$. To second order the Dunham coefficients are given by

$$Y_{kl} = \mu_C^{(k+2l)/2}U_{kl}\left[1 + m_{\mathrm{e}}\Delta^{a}_{kl}/M_a + m_{\mathrm{e}}\Delta^{b}_{kl}/M_b + \mathrm{O}\left(m_{\mathrm{e}}^2/M_i^2\right)\right], \qquad (48)$$

where m_{e} is the electron mass, M_a and M_b are the two atomic masses, and μ_C is the charge-modified reduced mass

$$\mu_C = M_a M_b/(M_a + M_b - Cm_{\mathrm{e}}), \qquad (49)$$

where C is the charge number of the molecule, so that the denominator in μ_C is the total mass. An important result of Watson (1980) is that the U_{kl} and the Δ^{i}_{kl} are nuclear mass independent constants. The correction represented by $\mathrm{O}(m_{\mathrm{e}}^2/M_i^2)$ in equation (48) is too small to be characterized experimentally for an isolated ground electronic state. However, if there are low lying excited electronic states such higher-order terms would become significant. Substituting equation (48) into equation (47) one obtains an equation that can be used in the simultaneous fitting of rotation-vibration energy levels for all isotopomers of a diatomic molecule. The result of such a fitting will be values for the constants U_{kl} and Δ^{i}_{kl}. Farrenq *et al.* (1991) make such a fitting for the isotopomers of CO.

Bunker and Moss (1980) show for a triatomic molecule how the perturbation theory contact transformation procedure can be applied to eliminate matrix elements between an isolated ground electronic state and the excited electronic states to give an effective rotation–vibration Hamiltonian. This effective rotation–vibration Hamiltonian contains nuclear mass dependent terms that correct for the adiabatic effects, and for the perturbing effect of all the excited electronic states.

1.2 The variation theory approach

In this approach we write the solution to the rovibronic wave equation as

$$\Psi_{\mathrm{rve},m}(r_{\mathrm{elec}}, U_{\mathrm{N}}) = \sum_{n'} \Phi^{m}_{\mathrm{rv},n'}(U_{\mathrm{N}})\Phi_{\mathrm{elec},n'}(r_{\mathrm{elec}}; \boldsymbol{R}_{\mathrm{N}}), \tag{50}$$

where $\Phi_{\mathrm{elec},n'}$ are a complete set of (orthonormal) solutions to the electronic wave equation (17), and the coefficient functions $\Phi^{m}_{\mathrm{rv},n'}(U_{\mathrm{N}})$ are to be determined. Substituting this expression into the rovibronic wave equation (8), multiplying on the left by $\Phi^{*}_{\mathrm{elec},n}$, and integrating over the electronic coordinates r_{elec}, we obtain the following set of coupled equations for the $\Phi^{m}_{\mathrm{rv},n'}(U_{\mathrm{N}})$:

$$\left[\hat{T}_{\mathrm{N}} + E_{\mathrm{elec},n}(\boldsymbol{R}_{\mathrm{N}}) - E_{\mathrm{rve},m}\right]\Phi^{m}_{\mathrm{rv},n}(\boldsymbol{R}_{\mathrm{N}}) + \sum_{n'} C_{nn'}\Phi^{m}_{\mathrm{rv},n'}(\boldsymbol{R}_{\mathrm{N}}) = 0, \tag{51}$$

where

$$C_{nn'} = \left\langle \Phi_{\mathrm{elec},n}\middle|\hat{T}'_{\mathrm{e}} + \hat{T}_{\mathrm{N}}\middle|\Phi_{\mathrm{elec},n'}\right\rangle. \tag{52}$$

Different levels of approximation are achieved depending on how the $C_{nn'}$ are dealt with.

If the $C_{nn'}$ are ignored entirely we have what is traditionally called 'the' BO approximation, which we can summarize by writing:

$$\Psi_{\mathrm{rve},m}(r_{\mathrm{elec}}, U_{\mathrm{N}}) = \Phi^{m}_{\mathrm{rv},n}(U_{\mathrm{N}})\Phi_{\mathrm{elec},n}(r_{\mathrm{elec}}; \boldsymbol{R}_{\mathrm{N}}), \tag{53}$$

where $\Phi_{\mathrm{elec},n}(r_{\mathrm{elec}}; \boldsymbol{R}_{\mathrm{N}})$ is the solution of the electronic wave equation:

$$\left[-\frac{\hbar^2}{2m_{\mathrm{e}}}\sum_{i=N+1}^{l}\nabla_i^2 + V(\boldsymbol{R}_{\mathrm{N}}, r_{\mathrm{elec}}) - E_{\mathrm{elec},n}(\boldsymbol{R}_{\mathrm{N}})\right]\Phi_{\mathrm{elec},n}(r_{\mathrm{elec}}; \boldsymbol{R}_{\mathrm{N}}) = 0, \tag{54}$$

and $\Phi^{m}_{\mathrm{rv},n}(U_{\mathrm{N}})$ is the solution of the rotation–vibration wave equation:

$$\left[-\frac{\hbar^2}{2}\sum_{i=2}^{N}\frac{\nabla_i^2}{m_i} + \frac{\hbar^2}{2M_{\mathrm{N}}}\sum_{i,j=2}^{N}\nabla_i\cdot\nabla_j + V_{\mathrm{BO},n}(\boldsymbol{R}_{\mathrm{N}}) - E_{\mathrm{rve},m}\right]\Phi^{m}_{\mathrm{rv},n}(\boldsymbol{R}_{\mathrm{N}}) = 0, \tag{55}$$

with the Born–Oppenheimer potential energy function $V_{\mathrm{BO},n}(\boldsymbol{R}_{\mathrm{N}})$ given by

$$V_{\mathrm{BO},n}(\boldsymbol{R}_{\mathrm{N}}) = E_{\mathrm{elec},n}(\boldsymbol{R}_{\mathrm{N}}), \tag{56}$$

which is isotopically independent.

If we only ignore off-diagonal elements of $C_{nn'}$ we have 'the adiabatic approximation'. In this approximation the rotation–vibration function is obtained from

$$\left[-\frac{\hbar^2}{2}\sum_{i=2}^{N}\frac{\nabla_i^2}{m_i}+\frac{\hbar^2}{2M_{\mathrm{N}}}\sum_{i,j=2}^{N}\nabla_i\cdot\nabla_j+V_{\mathrm{ad},n}(\boldsymbol{R}_{\mathrm{N}})-E_{\mathrm{rve},m}\right]\Phi^{m}_{\mathrm{rv},n}(\boldsymbol{R}_{\mathrm{N}})=0, \tag{57}$$

with the adiabatic potential energy function $V_{\mathrm{ad}}(\boldsymbol{R}_{\mathrm{N}})$ given by

$$\begin{aligned} V_{\mathrm{ad},n}(\boldsymbol{R}_{\mathrm{N}}) &= E_{\mathrm{elec},n}(\boldsymbol{R}_{\mathrm{N}})+C_{nn} \\ &= E_{\mathrm{elec},n}(\boldsymbol{R}_{\mathrm{N}})+\left\langle\Phi_{\mathrm{elec},n}\middle|\hat{T}'_{\mathrm{e}}+\hat{T}_{\mathrm{N}}\middle|\Phi_{\mathrm{elec},n}\right\rangle. \end{aligned} \tag{58}$$

The adiabatic potential energy function depends on isotope because of the presence of the nuclear masses in $\hat{T}'_{\mathrm{e}}+\hat{T}_{\mathrm{N}}$.

The full nonadiabatic calculation would involve making no approximations and including all $C_{nn'}$. This would give rise to an infinite number of coupled equations and each eigenfunction would be the infinite sum of product functions given in equation (50). However, in practice, this complete nonadiabatic calculation is never attempted. Calculations involve either isolated electronic states or situations in which two or three electronic states are close in energy and for which their interaction has to be treated explicitly.

Several of the chapters in this book are concerned with the study of the rotation–vibration energies in an isolated ground electronic state, and the BO approximation is assumed. This means that the rotation–vibration energies are obtained by solving

$$\left[-\frac{\hbar^2}{2}\sum_{i=2}^{N}\frac{\nabla_i^2}{m_i}+\frac{\hbar^2}{2M_{\mathrm{N}}}\sum_{i,j=2}^{N}\nabla_i\cdot\nabla_j+V_{\mathrm{BO}}(\boldsymbol{R}_{\mathrm{N}})-E_{\mathrm{rv},m}\right]\Phi^{m}_{\mathrm{rv}}(\boldsymbol{R}_{\mathrm{N}})=0, \tag{59}$$

where for the ground ($n=0$) electronic state we write

$$V_{\mathrm{BO}}(\boldsymbol{R}_{\mathrm{N}})=E_{\mathrm{elec},0}(\boldsymbol{R}_{\mathrm{N}})-E_{\mathrm{elec},0}(\boldsymbol{R}_{\mathrm{N}}{}^{0}) \tag{60}$$

with $\boldsymbol{R}^0_{\mathrm{N}}$ being the ground electronic state equilibrium nuclear configuration. However, the chapter by Yarkony and the chapter by Buenker *et al.* are particularly concerned with the situation when two or more electronic potential energy curves $E_{\mathrm{elec},n}(\boldsymbol{R}_{\mathrm{N}})$ come very close for certain internuclear separations in a diatomic molecule. In this case nonadiabatic effects due to the coupling of such close lying states are explicitly considered. Also the chapter by Jensen, Osmann and Bunker on the Renner effect, and the chapter by Barckholtz and Miller on the Jahn–Teller effect, consider situations in polyatomic molecules when two potential energy surfaces are degenerate at a particularly symmetrical nuclear configuration. Nonadiabatic effects have again to be explicitly introduced.

1.3 References

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