# The Adiabatic Born–Oppenheimer Approximation

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The validity of the Born–Oppenheimer theorem permits the separation of nuclear and electronic motion in the quantum-mechanical treatment of molecular systems.[1] This well-known theorem is often quoted in modern quantum-chemical textbooks, but rarely illustrated in detail [an exception being, *e.g.* ref. 1(*f*), which contains a very detailed discussion for the diatomic molecule], and its importance in the calculation of molecular vibrational frequencies *via ab initio* quantum-mechanical calculations is mostly overlooked. It is the purpose of this paper to draw attention to these applications as well as to the activity in the field, but it does not aim to constitute a detailed review paper. The necessary wave-mechanical background to understand this paper can be found in any modern textbook.[2]

## 1 Normal Vibrations and Interatomic Forces

In the normal treatment of molecular-vibrational problems[3] the potential which governs motions of the nuclei is taken to be *harmonic*. The general wave equation for the nuclear vibrations in a molecule is taken to be:

$$\frac{h^2}{8\pi^2}\sum \frac{1}{m_\alpha}\nabla_\alpha^{\,2}\phi + (E - V)\phi = 0\ , \tag{1}$$

where $\alpha$ refers to the nucleus $\alpha$ with mass $m_\alpha$ and $\nabla_\alpha^{\,2}$ is defined, as usual:

$$\nabla_\alpha^{\,2} = \frac{\partial^2}{\partial x_\alpha^{\,2}} + \frac{\partial^2}{\partial y_\alpha^{\,2}} + \frac{\partial^2}{\partial z_\alpha^{\,2}}\ . \tag{2}$$

Equation 1 can easily be transformed to the normal-co-ordinate form:

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[1] (*a*) M. Born and J. R. Oppenheimer, *Ann. Physik*, 1927, **84**, 457; (*b*) M. Born, *Festschrift Gött. Nachr. Math. Phys. Kl.*, 1951, **1**, 1; (*c*) W. D. Hobey and A. D. McLachlan, *J. Chem. Phys.*, 1960, **33**, 1695; (*d*) A. Dalgarno and R. McCarroll, *Proc. Roy. Soc.*, 1956, **A273**, 383; (*e*) A. D. Liehr, *Ann. Physics* (*New York*), 1957, **1**, 221; (*f*) J. C. Slater, 'Quantum Theory of Molecules and Solids', Vol. I, McGraw-Hill, New York, 1963; (*g*) R. Lefebvre and M. G. Sucre, *Internat. J. Quantum Chem. Symp.*, 1967, **1S**, 337.

[2] For example, (*a*) C. J. H. Schutte, 'The Wave Mechanics of Atoms, Molecules and Ions', Edward Arnold (Publishers), London, 1968; (*b*) F. L. Pilar, 'Elementary Quantum Chemistry', McGraw-Hill, New York, 1968.

[3] (*a*) See Ref. 2(*a*), Chapters 3, 12, and 14; (*b*) G. Herzberg, 'Spectra of Diatomic Molecules', D. van Nostrand Co., Princeton, 2nd edn., 1950; (*c*) G. Herzberg, 'Infrared and Raman Spectra', D. van Nostrand Co., Princeton, 1945; (*d*) E. B. Wilson, jun., J. C. Decius, and P. C. Cross, 'Molecular Vibrations', McGraw-Hill, New York, 1955.

$$\frac{h^2}{8\pi^2}\sum_{k}^{3N-6}\frac{\partial^2\phi}{\partial Q_k^2} + (E - \tfrac{1}{2}\sum_{k} f_{kk}\, Q_i^2)\phi = 0 \;, \qquad (3)$$

using a Taylor expansion of the vibrational-potential energy around the equilibrium position, referring the leading term to the minimum position and keeping only the second (harmonic) term. Equation 3 then splits smoothly into the separate $3N - 6$ vibrational Schrödinger equations:

$$\frac{h^2}{8\pi^2}\cdot\frac{\mathrm{d}^2\phi_{kv}}{\mathrm{d}Q_k^2} + (E_{kv} - \tfrac{1}{2} f_{kk}\, Q_k^2)\,\phi_{kv} = 0 \;, \qquad (4)$$

where $Q_k$ is the $k$-th normal co-ordinate and $\phi_{kv}$ the wave function describing the vibration of the $k$-th normal mode having a vibrational quantum number $v$ ($v = 0, 1, 2, \ldots\ldots$). Equation 4 is a harmonic-oscillator equation with solution:

$$E = (v_k + \tfrac{1}{2})h\nu_k \;. \qquad (5)$$

The harmonic potential-energy expression:

$$V = \tfrac{1}{2} f_{kk}\, Q_k^2 \;, \qquad (6)$$

generates the harmonic force constant:

$$f_{kk} = \frac{\mathrm{d}^2 V}{\mathrm{d}Q_k^2} \qquad (7)$$

and thus the *force* on each atom during the execution of the specific normal mode $Q_k$:*

$$F = -f_{kk}Q_k \;, \qquad (8)$$

$$\text{where } Q_k = \sum_{m=1}^{3N-6} a_{km}q_m \;, \qquad (9)$$

$q_m$ being the mass-weighted co-ordinates

$$q_1 = \sqrt{m_1}\,\Delta x_1;\; q_2 = \sqrt{m_1}\,\Delta y_1,\ \textit{etc.}, \qquad (10)$$

referred to the displacement co-ordinates $\Delta x_\alpha$, $\Delta y_\alpha$, $\Delta z_\alpha$ of each nucleus $\alpha$ during the execution of the vibration.

## 2 The Born–Oppenheimer Approximation

The computational difficulties of the general Schrödinger equation for a molecule:

$$\Bigg[-\sum_{\substack{\alpha\\ \text{(nuclei)}}}\frac{h^2}{8\pi^2 M_\alpha}\nabla_\alpha^2 - \sum_{\substack{i\\ \text{(electrons)}}}\frac{h^2}{8\pi^2 m_i}\nabla_i^2 + V(\mathbf{R}_\alpha, \mathbf{r}_i)\Bigg]\Psi = E\Psi(\mathbf{R}_\alpha, \mathbf{r}_i), \quad (11)$$

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*It is to be noted that in actual calculations the atoms must move along their normal-mode trajectories; see the last part of this review.

do not allow the exact evaluation of the molecular-vibrational problem. In normal molecular orbital calculations the motion of the nuclei is ignored, *i.e.* it is assumed that the electrons move so fast that they instantaneously adjust themselves to the nuclear motion. Equation 11 is accordingly simplified by assuming the nuclei to be clamped in positions given by the vectors $\mathbf{R}_\alpha'$, so that the first term in equation 11 is equal to zero, *i.e.* the Schrödinger equation describing the electronic motion and energy *in this specific nuclear configuration* is:

$$\left[-\sum_i \frac{h^2}{8\pi^2 m_i}\nabla_i^2 + V(\mathbf{R}_\alpha'; \mathbf{r}_i)\,\chi(\mathbf{R}_\alpha'; \mathbf{r}_i)\right] = E(\mathbf{R}_\alpha')\,\chi(\mathbf{R}_\alpha'; \mathbf{r}_i) \tag{12}$$

In this equation $V(\mathbf{R}_\alpha'; \mathbf{r}_i)$ is the total *coulombic energy* between the nuclei (N) and electrons (e) in this internuclear configuration $\mathbf{R}_\alpha'$:

$$V = V_{\mathrm{NN}} + V_{\mathrm{Ne}} + V_{\mathrm{ee}} \ , \tag{13}$$

and $\chi(\mathbf{R}_\alpha'; \mathbf{r}_i)$ and $E(\mathbf{R}_\alpha'; \mathbf{r}_i)$ are, respectively, the total electronic wave function and the total electronic energy. $E(\mathbf{R}_\alpha')$ is obviously a *minimum* at $\mathbf{R}' = R_e$, the equilibrium internuclear position. By shifting each nucleus $\alpha$ by arbitrary amounts $(\triangle x_\alpha, \triangle y_\alpha, \triangle z_\alpha)$ around the equilibrium internuclear position $R_e$ and calculating the resulting $E(\mathbf{R}_\alpha'; \mathbf{r}_i)$, a hypersurface $V(\mathbf{R}_\alpha')$ may be determined.

This is, perhaps, more easily visualised for the diatomic case where there are six nuclear co-ordinates $(\triangle x_1, \triangle y_1, \triangle z_1,$ *etc.*) but if the five rotations are excluded, only the internuclear distance $R$ is important in equation 12. The calculation of $E(\mathbf{R}')$ at various $R$ thus leads to the total-energy curve of the type given in Figure 1 for KF,[4] for seven internuclear distances $R$. At $R = R_e$ the nuclei are experiencing no nett forces towards each other, but at $R = 4{\cdot}400$ a.u. (marked 6 on the curve), the total energy of the molecule $(\mathrm{KF})_{R\,=\,4\cdot4}$ is higher than that of the molecule at the equilibrium position $(\mathrm{KF})_{R\,=\,4\cdot104}$. This means that there are nett forces acting upon the nuclei towards each other, pulling them as it were towards the position of equilibrium separation $R_e$. At point 2 ($R = 3{\cdot}95$ a.u.) the nuclei are experiencing nett forces away from each other. It is thus clear that one can regard the curve in Figure 1 as the graph of the potential-energy expression $E(\mathbf{R}_\alpha') = V(\mathbf{R}')$ which regulates the vibrational motion of the two nuclei with respect to each other; it is obvious that $V(\mathbf{R}')$ is not harmonic—in fact, it is very nearly described by a Morse-type potential function.

Generalisation then immediately leads to the vibrational Schrödinger equation:

$$\left[-\frac{h^2}{8\pi^2}\sum_\alpha \frac{1}{M_\alpha}\nabla_\alpha^2 + E(\mathbf{R}_\alpha')\right]\phi_v(\mathbf{R}_\alpha') = E_v\phi_v(\mathbf{R}_\alpha') \ , \tag{14}$$

where $\phi_v(\mathbf{R}_\alpha')$ is the vibrational wave function referring to the motion of the nuclei and $E_v$ the vibrational energy.

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[4] R. F. Matcha, *J. Chem. Phys.*, 1968, **49**, 1264.

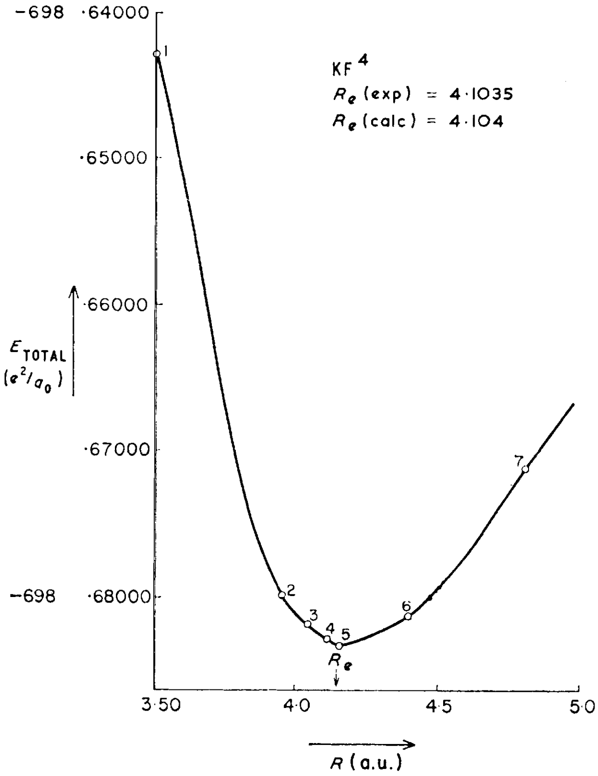

**Figure 1** *The variation of total energy* $E_{Total}$ *with interatomic distance* R *in* KF. (*The values are taken from the work of Matcha.*[4])

This approximation is valid if the substitution:

$$\Psi(\mathbf{R}_\alpha, \mathbf{r}_i) = \chi(\mathbf{R}_\alpha'; \mathbf{r}_i) \cdot \phi_v(\mathbf{R}_\alpha') \qquad (15)$$

into equation 11 does not yield residual terms which are large. It turns out that these residual terms are indeed negligibly small (Born–Oppenheimer approximation).

## 3 Solution of the Vibrational Problem: Diatomic Molecules

Direct solution of equation 14 for diatomic molecules, fitting the experimental points to an empirical equation in $R$, and substituting and solving for the vibrational eigenfunctions and eigenvalues (and hence for the vibrational frequencies of the transitions between the levels) is, in general, not possible. The general practice is to fit the points nearest to $R_e$ to a *parabolic potential* $V$. The value of the gradient at $R = R_e$ then yields $f_R$ (equation 7), from which follows:

$$\nu_R = \frac{1}{2\pi}\left(\frac{f_R}{\mu}\right)^{\frac{1}{2}} \tag{16}$$

This method is obviously not very accurate, and it is better to subject the points to a Dunham analysis[5] by expanding the potential energy around the equilibrium position $R_e$ in terms of a polynomial function of a dimensionless parameter $\xi$,[6]

$$\xi = \frac{R - R_e}{R_e} . \tag{17}$$

The evaluation of the Dunham constants gives $\omega_e$, $\omega_e x_e$, $\omega_e y_e$, *etc.* in the spectroscopic term-value equation:

$$G_v(\text{cm}^{-1}) = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 - \ldots , \tag{18}$$

where $\nu_e/c = \omega_e(\text{cm}^{-1})$. Matcha's analysis of KF[4] yields (all values in $\text{cm}^{-1}$):

$$\omega_e = 448{\cdot}5\ (442{\cdot}6);\ \omega_e x_e = 2{\cdot}484\ (2{\cdot}430);\ \omega_e y_e = 0{\cdot}04033;\ \omega_e z_e = 0{\cdot}000861;$$

the experimental values are given in brackets, where available. It is seen that this *ab initio* LCAO–SCF–Hartree–Fock calculation of Matcha yields the nearly correct molecular vibrational term values for the heavy molecule KF and thus definitely identifies the molecular (ionic) species found in the vapour of KF. The same approach was successfully applied to LiCl, NaF, and NaCl (see references in ref. 4).

It must be remembered that the individual $E(\mathbf{R}')$ values which were calculated (Figure 1) are not simply the sum over the energies of the one-electron occupied molecular orbitals $1\sigma$, $2\sigma$, . . . . . $1\pi$, $2\pi$, . . . . . . *etc.*, but are the *total energy values of the molecule at the various* $\mathbf{R}'$. Each $E(\mathbf{R}')$ is the sum of the following terms:

(i) the potential energy of interaction between electrons and the nuclei;
(ii) the potential energy of interaction between the electrons themselves;
(iii) the potential energy of internuclear repulsion; and
(iv) the kinetic energy of the electrons.

The break-down of the total energy into the kinetic energy $\bar{T}_e$ (of the electrons) and the potential energy of interaction $\bar{V}_e$ (nuclear repulsion not added) is given in Figure 2; the total energy is:

$$E_{\text{Total}} = \bar{T}_e + \bar{V}_e \tag{19}$$

According to the virial theorem, at the equilibrium position of a diatomic molecule the following relation holds:

$$-\frac{\bar{V}_e}{2\bar{T}_e} = 1 \tag{20}$$

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[5] (*a*) J. L. Dunham, *Phys. Rev* , 1932, **41,** 721; (*b*) A. D. McLean, *J. Chem. Phys.*, 1964, **40,** 2774; (*c*) R. M. Herman and S. Short, *J. Chem. Phys.*, 1968, **48,** 1266; (*d*) Ref. 4 and references therein.

[6] See equations 9—11 of R. L. Matcha, *J. Chem. Phys.*, 1967, **47,** 4595; in this paper the theory is applied to LiCl.

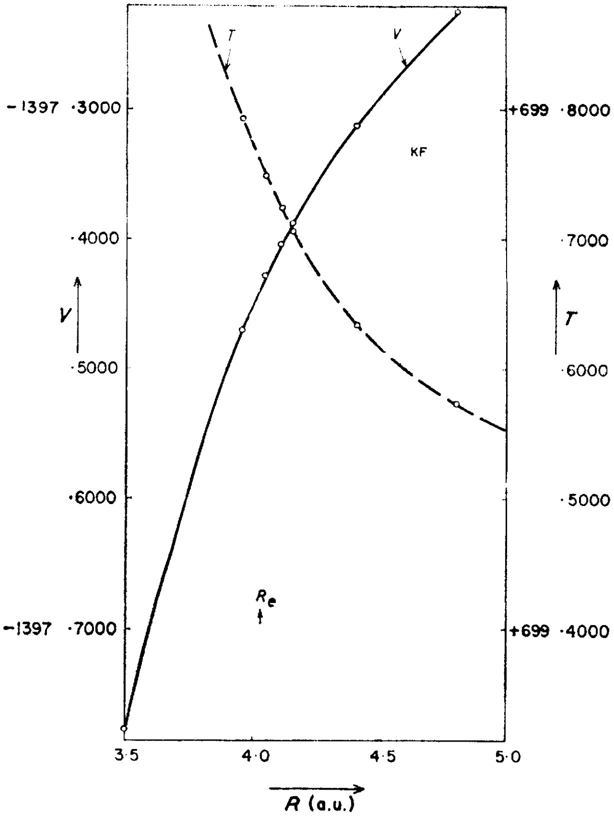

**Figure 2** *The variation of* $\overline{V}_e$ *and* $\overline{T}_e$ *with* R *for* KF. *See text for discussion.* (*Replotted from the results of Matcha.*[4])

In the case of KF, $-\overline{V}_e/2\overline{T}_e \approx 1{\cdot}0000$. Equation 20 follows from the expressions for a diatomic molecule

$$\overline{T}_e = -E(R) - R\left[\frac{dE(R)}{dR}\right], \tag{21}$$

$$\overline{V}_e = +2E(R) + R\left[\frac{dE(R)}{dR}\right] \tag{22}$$

at $R = R_e$, the gradient is zero, so that

$$\overline{T}_e = -E(R) \tag{23}$$

$$\overline{V}_e = +2E(R), \tag{24}$$

from which equation 20 follows. (Note that $E_{\mathrm{Total}}$ in the Born–Oppenheimer approximation includes the internuclear repulsion interaction!) Kolos and Wolniewicz[7] use equations 21 and 22 to calculate the $R_e$ at which $\mathrm{d}E(R)/\mathrm{d}R$ is equal to zero for the hydrogen molecule.

In its simplest form, the Hartree–Fock Method for a molecule utilises a single-determinant antisymmetrised product wave function of spin-orbitals of the type:

$$\Psi_i = \frac{1}{\sqrt{N!}} \left| \chi_1(1)\, \chi_2(2)\, \chi_3(3) \ldots\ldots \chi_N(N) \right| \tag{25}$$

The $\chi_i(i)$ form an orthonormal set of one-electron orbitals composed of the product of a space part, $\phi_i$, and a spin part, which can be either $\alpha$ or $\beta$. From equations 12 and 13 it is clear that the Hamiltonian operator $\mathscr{H}$ of the electronic problem in the Born–Oppenheimer framework is:

$$\mathscr{H} = T_{\mathrm{e}} + V_{\mathrm{ee}} + V_{\mathrm{Ne}} + V_{\mathrm{NN}} \ , \tag{26}$$

the $V$-terms being given by the appropriate coulombic terms:

$$V_{\mathrm{Ne}} = -\sum_{\mu,i} Z_\mu e^2/r_{\mu i} \ , \tag{27}$$

$$V_{\mathrm{ee}} = \sum_{i,j} e^2/r_{ij} \ , \tag{28}$$

$$V_{\mathrm{NN}} = \sum_{\mu\sigma} Z_\mu Z_\sigma (e^2/r_{\mu\sigma}) \ . \tag{29}$$

Equation 26 may be contracted to:

$$\mathscr{H} = \sum_i H_{\mathrm{N}}(i) + \sum_{i,j}(e^2/r_{ij}) \ , \tag{30}$$

where $H_{\mathrm{N}}(i)$ is the so-called 'core' Hamiltonian, and the last term the electron-repulsion term. The energy of the state with eigenfunction $\Psi_i$ is given by

$$E = \langle \Psi_i | \mathscr{H} | \Psi_i \rangle \ . \tag{31}$$

This is broken down by the substitution of equations 25 and 30 into two classes of integrals, *viz.*:

(i) the core integrals

$$I_i = \langle \chi_i | \mathscr{H}_{\mathrm{N}} | \chi_i \rangle \ , \tag{32}$$

(ii) the electron repulsion integrals:

$$(ij/kl) = \left\langle \chi_i \chi_j \left| \frac{e^2}{r_{12}} \right| \chi_k \chi_l \right\rangle \tag{33}$$

$$J_{ij} = (ii|jj); \ (i \neq j) \tag{34}$$

$$K_{ij} = (ij|ji); \ (i \neq j) \ . \tag{34a}$$

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[7] W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, 1966, **45**, 509.

Then it follows that:

$$E = \sum_{k}^{N} I_k + \tfrac{1}{2}\sum_{kl}^{N}(J_{kl} - K_{kl}) \ . \tag{35}$$

The forms of the individual orbitals $X_i$ (*i.e.* that of $\phi_i$, the space parts) are now determined *via* the variation method, keeping the condition of orthonormality on the set of $X_i$'s. This leads to the problem being simplified into a set of (apparently) one-electron problems, the Hartree–Fock set of equations:

$$\mathscr{F}(1)X_i(1) = \epsilon X(1) \ , \tag{36}$$

with the Hartree–Fock operator defined by:

$$\begin{aligned} \mathscr{F}(1) &= H_N(1) + \sum_j [J_j(1) - K_j(1)] \\ &= H_N(1) + G(1) \ . \end{aligned} \tag{37}$$

$G(1)$ is a one-electron operator (coulomb-exchange) which describes the repelling effects of all other electronic charges on the electron which is constrained to be in $X_N$. The eigenvalues of the one-electron Hartree–Fock operator $F(1)$ are then

$$\epsilon_i = I_i + \sum_j (J_{ij} - K_{ij}) \ . \tag{38}$$

This means that the total Hartree–Fock energy is, in terms of the orbital eigenvalues and the electron-repulsion integrals:

$$E = \sum_{i}^{N} \epsilon_i - \tfrac{1}{2}\sum_{i,j}^{N}(J_{ij} - K_{ij}) \ , \tag{39}$$

or

$$E = \tfrac{1}{2}\sum_{i}^{N}(\epsilon_i + I_i) \ . \tag{40}$$

This illustrates the statement above that the total Hartree–Fock energy is not simply the sum of the Hartree–Fock individual orbital energies—the core energies of equation 32 must be added to $\sum \epsilon_i$ or the electron-repulsion terms subtracted, as given by equations 39 and 40. Equation 37 is written here as if it were spin-independent. This is the case in which the term symbol of the molecule is $\Sigma$, *i.e.* there are $N$ electrons distributed in *pairs* with spin $\alpha$ and $\beta$ over the $N/2$ space orbitals $\{\phi_1, \phi_2, \ldots\ldots \phi_{N/2}\}$.) The Roothaan scheme, where the $\phi_i$ are approximated by the linear combination:

$$\phi_i = \sum_{k=1} C_{ki}\,\phi_k^0 \ , \tag{41}$$

leads to the same type of equations.[8]

There is the tendency to consider only the contribution of the Hartree–Fock orbital energy $\sum_i \epsilon_i$ and its variation with internuclear parameters in discussions

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[8] (*a*) C. J. J. Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69; (*b*) Ref. 1(*f*).

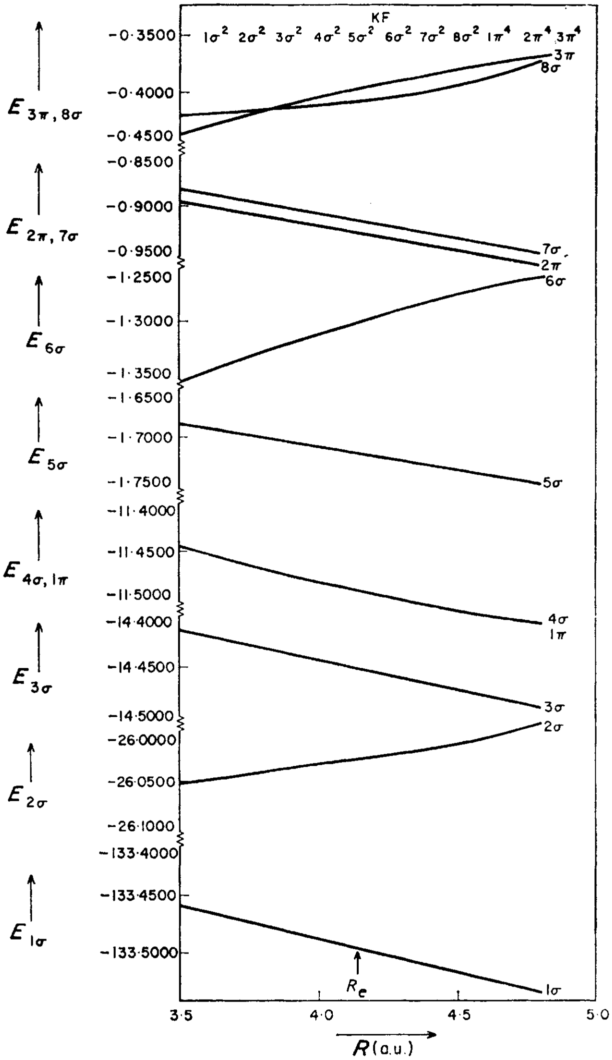

**Figure 3** *The variation of the orbital energies* $\epsilon_i$ *of* KF, *replotted from the results of Matcha.*[4] *See text.*

regarding the bonding situation in molecules. Thus, the variation of the orbital energies $E$ of KF, which is graphically shown in Figure 3, can be used in a discussion of the bonding between 3·5 and 4·8 a.u. This is not quite correct because, if one chooses to ignore the repulsion effects of equations 39 and 40, then

$$E_{\text{mol}} = 2\sum \epsilon_i < E_{\text{Hartree–Fock}} \tag{42}$$

at all values of $R$. The *forces* acting on the nuclei at all values of $R$ (excepting $R = R_e$) are thus due to *both* the one-orbital energies of the Hartree–Fock Scheme and the repulsion integrals $J_{ij}$ and $K_{ij}$. These forces determine the vibrational term values [$\omega_e(v + \frac{1}{2})$ + anharmonic terms] of equation 18, and thus the infrared transition frequencies of the molecule in the electronic state under consideration. To judge the rôle played by the sum of the orbital energies, the values of the $\epsilon_i$'s, $J_{ij}$, and $K_{ij}$ should be available for a set of selected values of $R$. The last two quantities are usually not tabulated in the papers dealing with these calculations, so that usually it is difficult to judge the exact 'origin of the potentials' which sum together to give a curve of the type of Figure 1. Most authors, however, give values for $\overline{V}_e$ and $\overline{T}_e$, so that the relative importance of the potential and kinetic energies may be evaluated (*e.g.* Figure 2). (It is worth noting that any $\epsilon_i$ is equal to the ionisation energy of the electron in that orbital by virtue of Koopmans' theorem.[9])

A deeper insight into the origin of the forces on the nuclei can be gained *via* the Hellmann–Feynman theorem; this will be the subject of a subsequent paper.

The only molecule for which the variation of $\epsilon_i$ (and thus $E_{\text{Hartree–Fock}}$) can be directly calculated, is $H_2^+$.[10] The calculated potential for $H_2^+$ is also amenable to a direct solution of the vibration–rotation problem.[11] The accurate variational study of Kolos and Wolniewicz[12] leads to a vibrational potential for the ground state of the $H_2$ molecule which can be used to integrate the vibrational–rotational Schrödinger equation numerically;[13] the results are very encouraging (the vibrational wave functions plotted for $H_2$ for $v = 0, 1, 2$, show clearly the anharmonicity of the vibration). The differences between the experimental values are +0·91, +0·80, +1·26, +0·85 cm$^{-1}$ respectively, for the $v = 0, 1, 2, 3$ states of $H_2$; the experimental values are 4161·13, 3925·97, 3695·24, and 3468·01 cm$^{-1}$ respectively.[14]

## 4 Polyatomic Molecules

More and more molecules are being treated by *ab initio* LCAO–MO calculations within the Hartree–Fock scheme. If such calculations are carried out over a range of internuclear distances in the clamped nuclei approximation, the resulting potential-energy curve can be used to calculate the normal modes of the molecule. In most cases it is not feasible to try to determine the whole potential-energy hypersurface of the molecule, but to make use of the concept of normal vibration as well as the symmetry of the molecule.

The easiest type of calculation is the calculation of the Hartree–Fock total energy of symmetrical molecules, and hence the potential energy governing the

[9] T. Koopmans, *Physica*, 1933, **1**, 104.
[10] H. Wind, *J. Chem. Phys.*, 1965, **42**, 2371 and references therein.
[11] H. Wind, *J. Chem. Phys.*, 1965, **43**, 2956.
[12] W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, 1964, **41**, 3663.
[13] L. Wolniewicz, *J. Chem. Phys.*, 1966, **45**, 515.
[14] G. Herzberg and L. L. Howe, *Canad. J. Phys.*, 1959, **37**, 636.

'breathing mode', by keeping the central (heavy) atom constant and bringing the lighter atoms adiabatically in along the main symmetry axes of the molecule. This means that the total Hartree–Fock energy of the molecule is effectively a one-dimensional function depending only upon the parameter $R$, the distance between the central atom and the peripheral atoms; the resulting potential curve is analogous to that of Figure 1, the orbital energy variation may be expressed as in Figure 3, and the virial partitioning of the energy proceeds as in Figure 2.

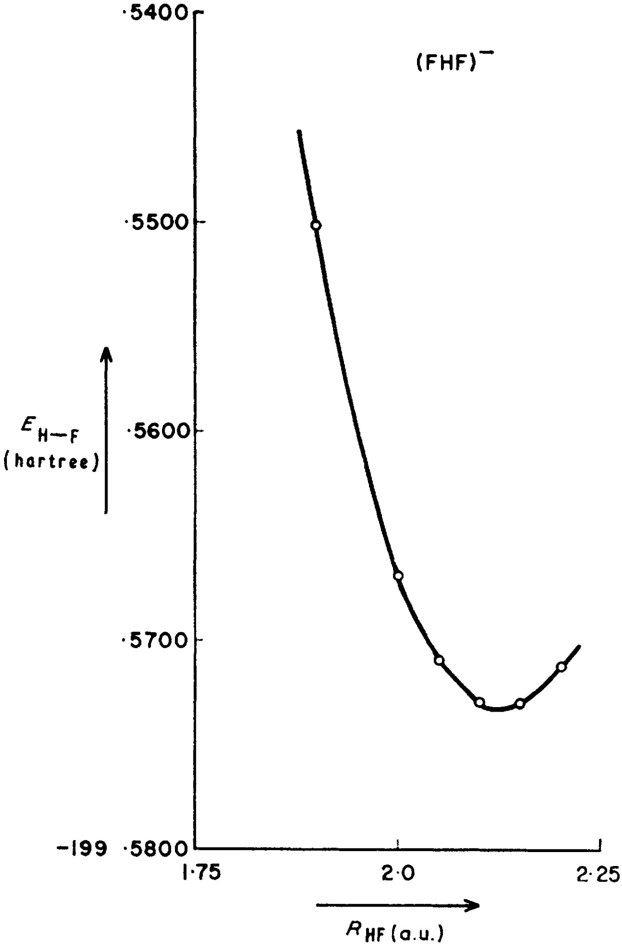

**Figure 4** *The Hartree–Fock potential energy of the stretching vibration of the linear ion* $(\mathrm{FHF})^-$. *The energy* E *was calculated at the following* F–H *separations* (*in* a.u.) *where the energies* (*in* hartrees) *are given in brackets:* 1·900 (−199·55042), 2·000 (−199·56707), 2·05 (−199·57113), 2·100 (−199·57296), 2·15 (−199·57291), *and* 2·200 (−199·57216). *Data from McLean and Yoshimine.*[15]

In Figure 4 the results of McLean and Yoshimine[15] for the breathing mode of the symmetrical bifluoride ion $(FHF)^-$ are plotted. It is seen that $E_{\text{Hartree–Fock}}$ goes through a minimum at an equilibrium value of $R_{\text{F–H}} \sim 2{\cdot}13$ a.u. ($= 1{\cdot}121$ Å) (the experimental value is $1{\cdot}13 \pm 0{\cdot}01$ Å[16]) and that there is no sign of a double-minimum in the potential. This means that the method described above (Dunham's Method) can be used to determine $\omega_e$ *etc.* The reader can also try to fit the four lowest points to a parabolic potential and to differentiate the resulting expression analytically to obtain the stretching force-constant $k$ and thus $\omega$. The McLean–Yoshimine tables can also be used to calculate the frequency of, *e.g.* $\nu_1$ of $CO_2$.

The same method can be applied for the breathing vibration of tetrahedral molecules, and encouraging results were obtained, although the absolute accuracy of the $E$ calculations was not large—see *e.g.* the calculations on $CH_4$, $SiH_4$, and $NH_4^+$.[17]

This method is not directly applicable to the stretching mode of unsymmetrical molecules like FCN, *etc.*, where the central atom moves during the 'stretching' normal mode. In such cases the atoms should be clamped along their actual normal-mode trajectories. A graph of the normal mode $Q$ *vs.* $E_{\text{Hartree–Fock}}$ should then be *similar* to Figures 1 and 4, and the frequency of the mode can be calculated.

In a very interesting ***ab initio*** LCAO–MO calculation of the electronic structure of the nitrous oxide molecule in both the NNO and NON configurations, as well as the azide ion $N_3^-$, Buenker and Peyerimhoff[18] determined the bending force constants. The bending force constant for NNO is $6{\cdot}8$ ($10^{-12}$ erg rad$^{-1}$) while the experimental value is $6{\cdot}9$. In the 'bending mode' calculated by Buenker and Peyerimhoff, the atoms do not follow the actual trajectories of the bending normal mode because the motion of the central atom was ignored. This means that the N–N and N–O distances were kept constant and that only the angle $\theta$ between the bonds was varied, *i.e.* the calculated 'bending mode' is not quite a normal mode, but a superposition of two or more of the molecular normal modes with phase angles $\gamma_i$. The calculated mode for the 'bending' in the ground state is nevertheless near enough to the real bending mode so that the general characteristics of the potential opposing a bending vibration become quite clear. The potential dependent upon the angle $\theta$ ($\equiv \mathrm{N\hat{N}O}$) is very much 'flatter' than those dependent upon the direct variation of the internuclear distances $R$. This means, in terms of equation 1, that the energy levels $E_{kv}$ of the bending mode are much closer spaced and that the corresponding transitions between them occur at much lower frequencies than the stretching frequencies in the same molecule. This is *qualitatively* shown in Figure 5, referred to the normal mode $Q$. (Note: the authors explain the almost universal occurrence of the most

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[15] A. D. McLean and M. Yoshimine, Supplement to the paper 'Computation of Molecular Properties and Structure', I.B.M. Journal of Research and Development, Nov. 1967.

[16] S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, 1952, **20**, 704; the F–F distance is $2{\cdot}26 \pm 0{\cdot}01$ Å, see L. Helmholz and M. T. Rogers, *J. Amer. Chem. Soc.*, 1939, **61**, 2590.

[17] E. Menna, R. Moccia, and L. Randaccio, *Theor. Chim. Acta*, 1966, **4**, 408.

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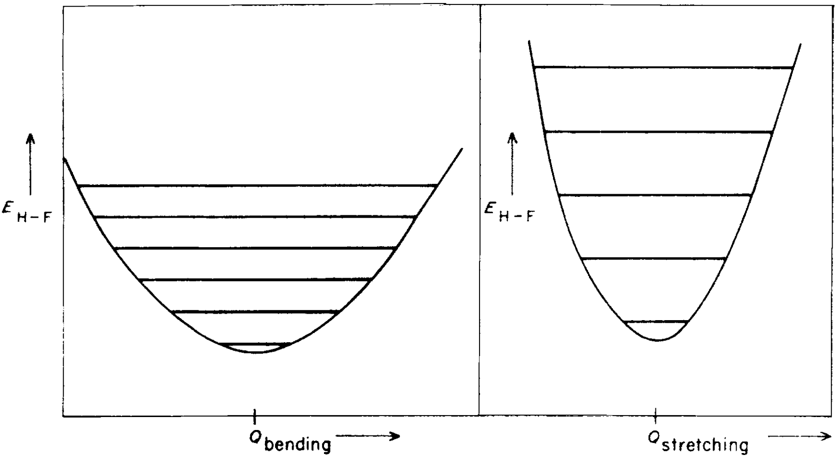

**Figure 5** *The bending and stretching potential curves (schematic). The bending curve is 'flatter' than the stretching curve, generates more closely-spaced eigenvalues and hence transitions occurring at lower frequencies (longer wavelengths).*

electropositive element in the middle of the triatomic molecule ABC in terms of the stabilisation of the $\pi$-MO's which are occupied; hence NNO forms and not NON.)

Even degenerate vibrational modes of the *ground electronic state* can be treated in this way, *i.e.* by clamping the nuclei on their actual normal-mode trajectories, so that the potential becomes effectively that of a one-dimensional (anharmonic) oscillator. No calculations have appeared using this principle.

It is thus clear that *ab initio* LCAO–MO calculations within the Hartree–Fock scheme and the Born–Oppenheimer approximation yield vibrational potential-energy curves which enable the theoretical determination of the molecular vibrational transition frequencies in the rotationless electronic ground state. The same procedure is applicable for non-degenerate vibrational modes of non-closed-shell molecules (*e.g.* the $\pi$-state of excited $CO_2$), but the Born–Oppenheimer approximation then breaks down for degenerate vibrations because of the coupling of vibrational angular momentum and the electronic angular momentum.[19]

The principles of force-constant-analysis are more fully discussed by Gerratt and Mills.[20]

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