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REGULAR ARTICLE

The separation of electronic and nuclear motion in the diatomic molecule

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Abstract The Schrödinger Coulomb Hamiltonian for electronic and nuclear motion in a diatomic molecule is presented and its effect upon functions which are products of functions of electronic and of nuclear variables is explicitly exhibited. Computational approaches to finding approximate solutions in such a basis are outlined.

1 Introduction

The Coulomb Hamiltonian operator for a system of N electrons and A atomic nuclei may be written as

$$\mathsf{H} = \sum_{g}^{A} \frac{\mathsf{p}_g^2}{2m_g} + \frac{e^2}{4\pi\epsilon_0} \sum_{g<h}^{A} \frac{Z_g Z_h}{r_{gh}} + \sum_{i}^{N} \left(\frac{\mathsf{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \sum_{g}^{A} \frac{Z_g}{r_{ig}} \right) + \frac{e^2}{4\pi\epsilon_0} \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{1}$$

This operator is essentially self-adjoint and bounded from below. It has, however, a completely continuous spectrum $[0, \infty]$. The fact that it is *completely* continuous is because of the centre-of-mass motion and to see any discrete spectrum this motion must be removed as

$$\mathsf{H} = \frac{\hbar^2}{2M_\mathrm{T}} \nabla^2(\xi) + \mathsf{H}' = \mathsf{T}_\xi + \mathsf{H}' \tag{2}$$

where ξ denotes the three-component cartesian coordinate of the centre-of-mass and M_T is the total mass of the system.

Since the centre-of-mass variable does not enter the potential energy term, the centre-of-mass motion may be separated off completely so that the eigenfunctions of H are of the form

$$T(\boldsymbol{\xi})\Psi(\mathbf{t}) \tag{3}$$

where $\Psi(\mathbf{t})$ is a wavefunction for the Hamiltonian $\mathsf{H}'(\mathbf{t})$ which we will refer to as the *translationally invariant* Hamiltonian. The $N + A - 1$ coordinates $\mathbf{t}_i$ are themselves translationally invariant and are typically chosen as a set of inter-particle distance vectors. The translationally invariant Hamiltonian is that which we must use when considering the separation of nuclear from electronic motion.

There are infinitely many possible choices of translationally invariant coordinates, so that the form of H' is not determined, but whatever coordinates are chosen the essential point is that all H' have the same spectrum. More detailed accounts of the spectral properties of the Coulomb Hamiltonian that will be cited below can be found in [1,2] and briefly but fully in [3]. It is the fact that the Coulomb potential, though unbounded, is small compared with the kinetic energy, that enables many of results to be proved. Interestingly enough, equivalent results in classical mechanics are not generally provable.

As a basis for quantum chemical calculations it is usually assumed that as a first step, electronic wave functions may be computed as solutions of the electronic Hamiltonian formed by allowing the nuclear masses in (1) to increase without limit:

$$\mathsf{H}^{\mathrm{elec}} = \sum_{i}^{N} \left(\frac{\mathsf{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \sum_{g}^{A} \frac{Z_g}{r_{ig}} \right) + \frac{e^2}{4\pi\epsilon_0} \sum_{i<j}^{N} \frac{1}{r_{ij}} + \frac{e^2}{4\pi\epsilon_0} \sum_{g<h}^{A} \frac{Z_g Z_h}{r_{gh}} \tag{4}$$

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and in practice the distances r_{ig} are considered as functions only of the electronic variables because the nuclei are considered to be clamped to yield a definite nuclear geometry for a calculation. The Hamiltonian is then perfectly well defined as a self-adjoint operator and the nuclear repulsion operator is simply an additive energy origin which plays no part in the dynamical problem. The Hamiltonian has very similar spectral properties to that of an atom or ion. However, if the nuclear positions are treated as variable and hence the r_{ig} and r_{gh} as multiplicative operators involving the nuclear variables, then the Hamiltonian ceases to be well defined because it contains no kinetic energy operators that can dominate the nuclear potential terms. The practical consequences of actually trying to let the nuclear masses increase without limit to produce an electronic Hamiltonian without clamping the nuclei seem to have been first investigated in the case of the hydrogen molecule ion-like system by Frolov [4]. He showed that what he called *adiabatic divergence* occurred in the spectrum, which is the expected consequence of the failure of the Hamiltonian to remain well defined. This failure is quite general and leaves open to question any attempt to justify the the Born–Oppenheimer approximation by invoking solutions to the electronic problem of the form

$$\mathsf{H}^{\text{elec}}\psi(\mathbf{r},\mathbf{R}) = E^{\text{elec}}(\mathbf{R})\psi(\mathbf{r},\mathbf{R}) \tag{5}$$

where it is assumed that the distances r_{ig} yielding the nuclear geometry variables $\mathbf{R}$ are multiplicative operators. In fact the problem can be properly specified only in terms of fixed choices of $\mathbf{R}$ and then by employing the theory of fiber bundles to cover the full space. This was first shown in the work of Combes and Seiler on the Born–Oppenheimer approximation for diatomic molecules [5] in the 1970s.

The enormous difference in mass between electrons and nuclei make it seem sensible to attempt solution of the problem by first treating the nuclear geometry $\mathbf{R}$ as a parameter for the description of the electronic motion specified in terms of the variables $\mathbf{r}$ and then using the results of the electronic calculations to provide a potential for nuclear motion. Although it might seem natural to attempt this starting with the classical electronic Hamiltonian (4), it is not really a satisfactory starting point. The energies and wavefunctions that result from its solution depend on the nuclear geometry only and not on the totality of nuclear variables. They are thus specified completely in terms of $3A-6$ variables or 1 variable in the case that $A=2$. It is thus necessary to "invent" 6 (or 5) more variables to tie this part of the problem to the full problem to be solved. The full problem would seem to offer no clues about how these required variables should be invented, except that they should be specified entirely in terms of the nuclear variables. On the other hand it is perfectly possible to transform the original Hamiltonian to yield a form in which the electronic motion is still recognizable and thus can be isolated to yield a base problem, and in which the relationship of the electronic part to that of the full problem is completely specified. This can be done by first specifying a set of translationally invariant coordinates that allow the separation of the translational motion to yield the Hamiltonian H' whose solutions are well defined. Then a coordinate frame can be embedded in the molecule by means of an orthogonal transformation specified in terms of three Euler angles leaving a set of $3A-6$ (or 1) internal variables which specify the nuclear geometry and are invariant under any orthogonal transformation of the original variables. Such a strategy is discussed in what follows in the case of a diatomic molecule.

2 The diatomic Hamiltonian

2.1 A form invariant under uniform translations of coordinates

In considering the diatomic molecule, for clarity of exposition consider first the construction just of a translationally invariant kinetic energy operator. A natural translationally invariant coordinate is the inter-nuclear distance vector

$$\mathbf{t}^{\text{n}} = \mathbf{x}_a - \mathbf{x}_b \tag{6}$$

where the laboratory nuclear coordinates are denoted $\mathbf{x}_a$ and $\mathbf{x}_b$ with masses m_a and m_b and charges Z_a and Z_b. There is however no equally natural set of translationally invariant electronic coordinates. A possible choice is

$$\mathbf{t}_i = \mathbf{x}_i + v_{ai}\mathbf{x}_a + v_{bi}\mathbf{x}_b, \quad i = 1, 2, \ldots N, \quad v_{ai} + v_{bi} = -1 \tag{7}$$

where $\mathbf{x}_i$ is the laboratory coordinate of the i−th electron.

The inverse transformation is

$$\begin{aligned} \mathbf{x}_a &= m_b M^{-1}\mathbf{t}^{\text{n}} + \mathbf{X} \\ \mathbf{x}_b &= -m_a M^{-1}\mathbf{t}^{\text{n}} + \mathbf{X} \\ \mathbf{x}_i &= \mathbf{t}_i + \frac{(m_a v_{bi} - m_b v_{ai})}{M}\mathbf{t}^{\text{n}} + \mathbf{X} \end{aligned} \tag{8}$$

where $M = m_a + m_b$ and $\mathbf{X} = M^{-1}(m_a\mathbf{x}_a + m_b\mathbf{x}_b)$.

The centre of mass coordinate is

$$\mathbf{X}_T = \mathbf{X} + \frac{m}{M_T}\sum_{i=1}^{N}\mathbf{t}_i + \frac{m}{M_T M}\sum_{i=1}^{N}(m_a v_{bi} - m_b v_{ai})\mathbf{t}^{\text{n}} \tag{9}$$

where m is the electron and M_T the total mass.

For any choice of translationally invariant coordinates the part of the Hamiltonian involving the centre of mass motion may be separated off and the remaining operator consists of a kinetic energy operator in three parts and a potential operator. The kinetic energy operator will have the same structure no matter what set of translationally invariant coordinates is chosen, given that a distinction is to be made between electronic and nuclear coordinates. However, the details, such as reduced masses, will vary according to the choice. The form of the potential operator will depend entirely on the choice. Choosing the translationally invariant coordinates as in (6) and (7) the kinetic energy operator becomes

$$\mathsf{K}^{\mathrm{e}}(\mathbf{t}) + \mathsf{K}^{\mathrm{n}}(\mathbf{t}^{\mathrm{n}}) + \mathsf{K}^{\mathrm{en}}(\mathbf{t}^{\mathrm{n}}, \mathbf{t}) \tag{10}$$

Here, using $\vec{\nabla}$ as the usual vector gradient operator,

$$\mathsf{K}^{\mathrm{e}}(\mathbf{t}) = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla^2(\mathbf{t}_i) - \frac{\hbar^2}{2}\sum_{i,j=1}^{N}\frac{1}{\overline{\mu}_{ij}}\vec{\nabla}(\mathbf{t}_i)\cdot\vec{\nabla}(\mathbf{t}_j) \tag{11}$$

$$1/\overline{\mu}_{ij} = (v_{ai}v_{aj}/m_a + v_{bi}v_{bj}/m_b) \tag{12}$$

and

$$\mathsf{K}^{\mathrm{n}}(\mathbf{t}^{\mathrm{n}}) = -\frac{\hbar^2}{2\mu_{ab}}\vec{\nabla}^2(\mathbf{t}^{\mathrm{n}}) \tag{13}$$

in which μ_{ab} is just the standard reduced mass $m_a m_b/(m_a + m_b)$.

Finally

$$\mathsf{K}^{\mathrm{en}}(\mathbf{t}^{\mathrm{n}}, \mathbf{t}) = -\frac{\hbar^2}{2}(\vec{\nabla}(\mathbf{t}^{\mathrm{n}})\cdot\sum_{j=1}^{N}\frac{1}{\mu_j}\vec{\nabla}(\mathbf{t}_j) + \sum_{j=1}^{N}\frac{1}{\mu_j}\vec{\nabla}(\mathbf{t}_j)\cdot\vec{\nabla}(\mathbf{t}^{\mathrm{n}})) \tag{14}$$

with

$$\frac{1}{\mu_j} = \frac{v_{aj}}{m_a} - \frac{v_{bj}}{m_b} \tag{15}$$

Although the sign of this inverse reduced mass (15) depends upon the arbitrary choice made in labeling the nuclei, the other choice would result in the chosen form for $\mathbf{t}^{\mathrm{n}}$ being replaced by its negative, leaving (14) invariant as required. This operator vanishes when the elements on the right in (15) are equal for all $j = 1, 2, \ldots N$.

The inter-particle coordinates needed to form the potential operator are

$$\begin{aligned}\mathbf{x}_i - \mathbf{x}_j &= \mathbf{t}_i - \mathbf{t}_j + M^{-1}(m_a(v_{bi} - v_{bj}) - m_b(v_{ai} - v_{aj}))\mathbf{t}^{\mathrm{n}} \\ &= \mathbf{r}_{ij}(\mathbf{t}^{\mathrm{n}})\end{aligned} \tag{16}$$

$$\mathbf{x}_i - \mathbf{x}_a = \mathbf{t}_i + M^{-1}(m_a v_{bi} - m_b(v_{ai} + 1))\mathbf{t}^{\mathrm{n}} = \mathbf{r}_{ia}(\mathbf{t}^{\mathrm{n}}) \tag{17}$$

$$\mathbf{x}_i - \mathbf{x}_b = \mathbf{t}_i + M^{-1}(m_a(v_{bi} + 1) - m_b v_{ai})\mathbf{t}^{\mathrm{n}} = \mathbf{r}_{ib}(\mathbf{t}^{\mathrm{n}}) \tag{18}$$

The potential energy also has three parts but these will be treated together for the time being as:

$$\mathsf{V}(\mathbf{t}) = \frac{e^2}{8\pi\epsilon_0}{\sum_{i,j=1}^{N}}'\frac{1}{r_{ij}(R)} + \frac{e^2}{4\pi\epsilon_0}\frac{Z_a Z_b}{R} - \frac{e^2}{4\pi\epsilon_0}\sum_{j=1}^{N}\left(\frac{Z_a}{r_{ia}(R)} + \frac{Z_b}{r_{ib}(R)}\right) \tag{19}$$

where $R = |\mathbf{t}^{\mathrm{n}}|$ and $r_{ij}(R) = |\mathbf{r}_{ij}(\mathbf{t}^{\mathrm{n}})|$ and similarly for the other distances.

The translationally invariant angular momentum operator may be written as

$$\mathsf{J}(\mathbf{t}) = \frac{\hbar}{i}\left(\hat{\mathbf{t}}^{\mathrm{n}}\frac{\partial}{\partial\mathbf{t}^{\mathrm{n}}} + \sum_{i=1}^{N}\hat{\mathbf{t}}_i\frac{\partial}{\partial\mathbf{t}_i}\right) \tag{20}$$

where $\partial/\partial\mathbf{t}^{\mathrm{n}}$ denotes the 3 by 1 column matrix of first derivatives and

$$\hat{\mathbf{t}}_i = \begin{pmatrix} 0 & -t_{zi} & t_{yi} \\ t_{zi} & 0 & -t_{xi} \\ -t_{yi} & t_{xi} & 0 \end{pmatrix} \tag{21}$$

In future a position operator symbol with a caret over it will denote a skew-symmetric matrix of components like (21).

2.2 A form invariant under orthogonal coordinate transformations

Let the internuclear distance vector be written in the polar coordinates (R, β, α) where $t_z^{\mathrm{n}} = R\cos\beta$. Then the orthogonal matrix

$$\mathbf{C} = \begin{pmatrix} \cos\beta\cos\alpha & -\sin\alpha & \sin\beta\cos\alpha \\ \cos\beta\sin\alpha & \cos\alpha & \sin\beta\sin\alpha \\ -\sin\beta & 0 & \cos\beta \end{pmatrix} \tag{22}$$

is such that

$$\mathbf{r}^{\mathrm{n}} = \mathbf{C}^T\mathbf{t}^{\mathrm{n}} = \begin{pmatrix} 0 \\ 0 \\ R \end{pmatrix} \tag{23}$$

and the remaining cartesian variables may be transformed to variables in the frame defined by $\mathbf{C}$ as

$$\mathbf{r}_i = \mathbf{C}^T\mathbf{t}_i, \quad i = 1, 2, \ldots N \tag{24}$$

We can now eliminate the derivatives with respect to t_γ^{n}, $\gamma = x, y, z$ in favour of those with respect to R, β and α. Following [6] this yields

$$\frac{\partial}{\partial t_\gamma^{\mathrm{n}}} = \frac{C_{\gamma x}}{R}\left(\frac{\partial}{\partial\beta} - \frac{i}{\hbar}\mathsf{l}_y\right) + \frac{C_{\gamma y}}{R}\left(\csc\beta\frac{\partial}{\partial\alpha} - \cot\beta\frac{i}{\hbar}\mathsf{l}_z + \frac{i}{\hbar}\mathsf{l}_x\right) + C_{\gamma z}\frac{\partial}{\partial R} \tag{25}$$

Here

$$\mathsf{l} = \sum_{i=1}^{N}\mathsf{l}(i) = \frac{\hbar}{i}\sum_{i=1}^{N}\hat{\mathbf{r}}_i\frac{\partial}{\partial\mathbf{r}_i} \tag{26}$$

The operator l is composed of the three components of the electronic angular momentum expressed in the frame defined by $\mathbf{C}$.

Equation (25) may be rewritten as

$$\frac{\partial}{\partial \mathbf{t}^{\mathrm{n}}} = \mathbf{C}\frac{\partial}{\partial \mathbf{R}}$$

where $\partial/\partial\mathbf{R}$ denotes the 3 by 1 column matrix of the components on the right of (25). In the same notation

$$\frac{\partial}{\partial \mathbf{t}_i} = \mathbf{C}\frac{\partial}{\partial \mathbf{r}_i} \tag{27}$$

When expressed in internal coordinates, the operators $\partial/\partial\mathbf{t}^{\mathrm{n}}$ and $\partial/\partial\mathbf{t}_i$ do not commute so the ordering of operators shown in (14) must be maintained.

The total translationally invariant angular momentum becomes

$$\mathsf{J}(\mathbf{t}) = |\mathbf{C}|\mathbf{C}\left(\frac{\hbar}{i}\hat{\mathbf{r}}^{\mathrm{n}}\frac{\partial}{\partial \mathbf{R}} + \mathbf{l}\right) = |\mathbf{C}|\mathbf{C}\mathsf{J}(\mathbf{r}) \tag{28}$$

and since $\mathbf{C}$ is a proper rotation then $|\mathbf{C}|$ is $+1$ and may be ignored in what follows.

The components of the total angular momentum expressed in the frame defined by $\mathbf{C}$ are

$$\mathsf{J}_x(\mathbf{r}) = -\frac{\hbar}{i}\csc\beta\frac{\partial}{\partial\alpha} + \cot\beta\,\mathsf{l}_z, \quad \mathsf{J}_y(\mathbf{r}) = \frac{\hbar}{i}\frac{\partial}{\partial\beta}, \quad \mathsf{J}_z(\mathbf{r}) = \mathsf{l}_z \tag{29}$$

In what follows these components will be denoted simply as J_γ and called the components of pseudo-angular momentum because of their unusual form and because they do not satisfy standard commutation conditions.

The translationally invariant kinetic energy operators can now be rewritten in terms of the new coordinates. The electronic part (11) becomes

$$\mathsf{K}^{\mathrm{e}}(\mathbf{t}) \to -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla^2(\mathbf{r}_i) - \frac{\hbar^2}{2}\sum_{i,j=1}^{N}\frac{1}{\overline{\mu}_{ij}}\vec{\nabla}(\mathbf{r}_i)\cdot\vec{\nabla}(\mathbf{r}_j) \tag{30}$$

The nuclear part (13) becomes

$$\mathsf{K}^{\mathrm{n}}(\mathbf{t}^{\mathrm{n}}) \to -\frac{\hbar^2}{2\mu_{ab}R^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R} + \frac{1}{2\mu_{ab}R^2}\mathsf{D}_1(\alpha,\beta,\mathbf{r}) \tag{31}$$

and the interaction part (14) becomes

$$\mathsf{K}^{\mathrm{en}}(\mathbf{t}^{\mathrm{n}},\mathbf{t}) \to \frac{\hbar}{i}\left(\frac{\partial}{\partial R}\right)\mathsf{v}_z + \frac{1}{2R}\mathsf{D}_2(\alpha,\beta,\mathbf{r}) \tag{32}$$

where the velocity operator is

$$\mathsf{v} = \frac{\hbar}{i}\sum_{j=1}^{N}\frac{1}{\mu_j}\vec{\nabla}(\mathbf{r}_j) \tag{33}$$

This operator is unchanged by a change of nuclear variable labeling because such a change induces a change of $\mathbf{C}$ to $-\mathbf{C}$ and hence of $\mathbf{r}_i$ to $-\mathbf{r}_i$.

The operators D_i depend only on the Eulerian angles and their derivatives and the electronic coordinates and their derivatives. They may be written in many different ways. Using the angular momentum operators, for example, they become

$$\mathsf{D}_1(\alpha,\beta,\mathbf{r}) = \left[(\mathsf{J}_x - \mathsf{l}_x)^2 + (\mathsf{J}_y - \mathsf{l}_y)^2 + \frac{\hbar}{i}\cot\beta(\mathsf{J}_y - \mathsf{l}_y)\right]$$

and

$$\begin{aligned}\mathsf{D}_2(\alpha,\beta,\mathbf{r}) = {} & \frac{2\hbar}{i}\mathsf{v}_z + \left(\mathsf{J}_y - \mathsf{l}_y + \frac{\hbar}{i}\frac{\cot\beta}{2}\right)\mathsf{v}_x \\ & + \mathsf{v}_x\left(\mathsf{J}_y - \mathsf{l}_y + \frac{\hbar}{i}\frac{\cot\beta}{2}\right) \\ & + (\mathsf{J}_x - \mathsf{l}_x)\mathsf{v}_y + \mathsf{v}_y(\mathsf{J}_x - \mathsf{l}_x))\end{aligned}$$

but other forms may be found in [6,7] and in [8] for instance. For the time being however no particular choice need be made. In working with $\mathsf{D}_2(\alpha.\beta,\mathbf{r})$ the order of the operators is important because the electronic operators do not commute.

The potential energy operator remains just as is given in (19) but will from now on be written as $\mathsf{V}(R,\mathbf{r})$ to emphasize that it does not depend upon the orientation of the internuclear axis.

The full Hamiltonian for the problem $\mathsf{H}(\mathbf{R},\mathbf{r})$ is then just the sum of the right sides of (30), (31), (32) and (19) and the volume element for integration is

$$R^2\sin\beta\, dR\, d\beta\, d\alpha\, d\mathbf{r}$$

Using standard angular momentum results, the angular motion can be dealt with by choosing a solution of the form

$$\Phi^J_{pmn}(\alpha,\beta,R,\mathbf{r}) = \sqrt{\frac{1}{2\pi}}e^{in\alpha}\sqrt{\frac{2}{2J+1}}d^J_{nm}(\beta)\psi^J_{pm}(R,\mathbf{r}) \tag{34}$$

where d^J_{nm} is a term in a standard rotation matrix element as defined in [9] or equivalently in [10]. The subscript p on the wave function ψ^J_{pm} will be left uninterpreted for the time being. Denoting the normalisation factor in (34) by N_J and with ψ^J_{pm} chosen to be an eigenfunction of l_z with eigenvalue $\hbar m$ then

$$\begin{aligned}\mathsf{D}_1\Phi^J_{pmn} \to {} & -\hbar^2 N_J e^{in\alpha} \\ & \Big[d^J_{nm}(\beta)(m(m+1) - J(J+1) - \mathsf{l}^+\mathsf{l}^-/\hbar^2) \\ & + c^+_{Jm}d^J_{nm+1}(\beta)\mathsf{l}^+/\hbar + c^-_{Jm}d^J_{nm-1}(\beta)\mathsf{l}^-/\hbar\Big]\psi^J_{pm}\end{aligned} \tag{35}$$

and

$$\begin{aligned}\mathsf{D}_2\Phi^J_{pmn} \to {} & \frac{\hbar}{i}N_J e^{in\alpha}\Big[d^J_{nm}(\beta)(\mathsf{v}^+\mathsf{l}^- - \mathsf{v}^-\mathsf{l}^+)/\hbar \\ & - c^+_{Jm}d^J_{nm+1}(\beta)\mathsf{v}^+ + c^-_{Jm}d^J_{nm-1}(\beta)\mathsf{v}^-\Big]\psi^J_{pm}\end{aligned} \tag{36}$$

with

$$c^{\pm}_{Jm} = [J(J+1) - m(m\pm 1)]^{\frac{1}{2}} \tag{37}$$

The operators $\mathsf{l}^{\pm}$ are the standard raising and lowering operators and the $\mathsf{v}^{\pm}$ are defined just like $\mathsf{l}^{\pm}$ but using the components of the velocity operator. It should noted that the phase conventions adopted here are not the same as those used in [7] so that there are some sign differences between this work and that.

Although l^2 does not commute with the Hamiltonian it would be possible to require that the trial wavefunction be an eigenfunction of l^2 and if this were done then explicit expressions could be obtained for the effects of the raising and lowering operators, but to do so would constrain the form of wavefunction too strongly for our purposes.

The angular motion can be dealt with by multiplying each of (35) and (36) from the left by $\Phi^{J'}_{p'm'n'}$ and integrating over the angular coordinates. The resulting matrix elements are diagonal in n and J but, to save writing, this will not be explicitly noted and the index n will be suppressed in what follows because, in the absence of fields, the energy does not depend on n.

The matrix elements of the effective Hamiltonian diagonal in m for any $p'p$ choice are

$$\begin{aligned}\mathsf{H}_{p'm,pm} = \mathsf{H}^{\mathrm{e}}_{p'm,pm} &+ \frac{1}{2iR}\langle\psi^J_{p'm}|(\mathsf{v}^+\mathsf{l}^- - \mathsf{v}^-\mathsf{l}^+)|\psi^J_{pm}\rangle\\ &+\frac{\hbar^2}{2\mu_{ab}R^2}\langle\psi^J_{p'm}|J(J+1)-m(m+1)|\psi^J_{pm}\rangle\\ &+\frac{1}{2\mu_{ab}R^2}\langle\psi^J_{p'm}|\mathsf{l}^+\mathsf{l}^-)|\psi^J_{pm}\rangle\\ &+\frac{\hbar}{i}\langle\psi^J_{p'm}|\left(\frac{\partial}{\partial R}\right)\mathsf{v}_z|\psi^J_{pm}\rangle\\ &-\frac{\hbar^2}{2\mu_{ab}R^2}\langle\psi^J_{p'm}|\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}|\psi^J_{pm}\rangle \qquad (38)\end{aligned}$$

where

$$\begin{aligned}\mathsf{H}^{\mathrm{e}}_{p'm,pm} = &-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\langle\psi^J_{p'm}|\nabla^2(\mathbf{r}_i)|\psi^J_{pm}\rangle\\ &-\frac{\hbar^2}{2}\sum_{i,j=1}^{N}\frac{1}{\overline{\mu}_{ij}}\langle\psi^J_{p'm}|\vec{\nabla}(\mathbf{r}_i)\cdot\vec{\nabla}(\mathbf{r}_j)|\psi^J_{pm}\rangle\\ &+\langle\psi^J_{p'm}|\mathsf{V}(R,\mathbf{r})|\psi^J_{pm}\rangle \qquad (39)\end{aligned}$$

while the matrix elements off-diagonal in m are

$$\begin{aligned}&\mathsf{H}_{p'm+1,pm}\\ &= -c^{+}_{Jm}\left\langle\psi^J_{p'm+1}|\left(\frac{\hbar}{2\mu_{ab}R^2}\mathsf{l}^+ + \frac{\hbar}{2iR}\mathsf{v}^+\right)|\psi^J_{pm}\right\rangle \qquad (40)\end{aligned}$$

$$\begin{aligned}&\mathsf{H}_{p'm-1,pm}\\ &= -c^{-}_{Jm}\left\langle\psi^J_{p'm-1}|\left(\frac{\hbar}{2\mu_{ab}R^2}\mathsf{l}^- - \frac{\hbar}{2iR}\mathsf{v}^-\right)|\psi^J_{pm}\right\rangle \qquad (41)\end{aligned}$$

For any fixed choice of p and p' this system of equations generates a $2J+1$ dimensional secular problem which determines $2J+1$ eigenvalues ${}^{J}E_{p,p',t}$.

3 Isolating the electronic motion

From (39) the Hamiltonian

$$\begin{aligned}\mathsf{H}^{\mathrm{e}} = &-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla^2(\mathbf{r}_i) - \frac{\hbar^2}{2}\sum_{i,j=1}^{N}\frac{1}{\overline{\mu}_{ij}}\vec{\nabla}(\mathbf{r}_i)\cdot\vec{\nabla}(\mathbf{r}_j)\\ &+\mathsf{V}(R,\mathbf{r}) \qquad (42)\end{aligned}$$

can be extracted. Let us call this Hamiltonian the *fixed frame electronic* (FFE) Hamiltonian. Notice it is perfectly possible to specify R as a constant in this Hamiltonian, effectively clamping the nuclei, without requiring that the nuclear masses increase without limit. Were the nuclear masses to increase without limit the second kinetic energy term, the so-called *mass-polarization* term, would vanish. It is not, however, quite the usual clamped nuclei one. Because we have chosen to discuss a diatomic and thus required that the electronic function is an eigenfunction of l_z there is an extra restriction on the form of the electronic wavefunction. This restriction would not arise in the general case and can be regarded as a matter of no importance. There are however other reasons: the presence of the mass-polarization term and the possible presence of the nuclear variable R in the electron-repulsion term. The mass-polarization term could certainly be included by a simple extension of the usual numerical apparatus of a standard fixed nuclei calculation and, in any case, is probably a small term and so can be treated as a perturbation. So no issue of principle is involved here but the nuclear variable problem is more tricky.

Looking at the inter-electronic distance formula (16) it is seen that the internuclear distance will disappear if the choice $v_{ai} = v_{bi}$ for all i is made. In the original work of Kołos the electronic origin was taken at the mid-point of the internuclear separation so that this condition was satisfied and thus

$$\frac{1}{\overline{\mu}_{ij}} = \frac{1}{4\mu_{ab}}, \quad \frac{1}{\mu_j} = \frac{m_b - m_a}{2m_a m_b} \qquad (43)$$

and

$$\mathbf{t}_i = \mathbf{x}_i - \frac{1}{2}(\mathbf{x}_a + \mathbf{x}_b) \qquad (44)$$

$$\mathbf{x}_i = \mathbf{t}_i + \frac{(m_b - m_a)}{2M}\mathbf{t}^{\mathrm{n}} + \mathbf{X} \qquad (45)$$

so that

$$(\mathbf{x}_a - \mathbf{x}_j) = \left(\frac{\mathbf{t}^{\mathrm{n}}}{2} - \mathbf{t}_j\right), \quad (\mathbf{x}_b - \mathbf{x}_j) = -\left(\frac{\mathbf{t}^{\mathrm{n}}}{2} + \mathbf{t}_j\right) \qquad (46)$$

and

$$r_{ij} = |\mathbf{t}_j - \mathbf{t}_i|$$

The form of the inter-electronic distance is exactly thus the same as it is in clamped nuclei calculations. Furthermore if $\mathbf{t}^{\mathrm{n}}$ is treated as a constant specifying an origin, then the electron-nucleus distances are of exactly the same form as in a clamped nuclei calculation. Thus in this case, provided that the mass polarization term is ignored, the usual clamped nuclei electronic structure calculations can be fitted into the full problem and this remains the case whenever the electronic origin is chosen as the centre-of-nuclear mass.

Let us, however, consider the long-range behaviour of the electron-nucleus potential terms here. As $\mathbf{t}^{\mathrm{n}}$ becomes very large, the nuclear repulsion term becomes very small and, for any fixed values for the $\mathbf{t}_i$, the electron-nucleus attraction terms become small too, while the electronic repulsion terms remain constant. Thus the asymptotes of the problem so formulated are a pair of bare nuclei with the ionized electrons referred to a point midway between them. This is clearly not the sort of asymptote for which one is likely to be looking in a potential surface calculation. This is also general. If the translationally invariant electronic coordinates are settled, that is, if they are left unchanged by change of nuclear variables, then individual "atoms" will not emerge at the asymptotes from a set of the nuclei with the same masses.

To let a pair of neutral atoms emerge at the asymptotes it would be reasonable to define the v_{ai} and v_{bi} so that

$$\begin{aligned}\mathbf{t}'_i &= \mathbf{x}_i - \mathbf{x}_a, \quad i = 1, 2, \ldots, Z_a\\ \mathbf{t}'_i &= \mathbf{x}_i - \mathbf{x}_b, \quad i = Z_a + 1, \ldots, N\end{aligned} \tag{47}$$

The translationally invariant electronic coordinates so defined are not settled under nuclear permutations. The inverse of this transformation for the nuclei is as above in (9) while that for the electrons is

$$\begin{aligned}\mathbf{x}_i &= \mathbf{t}'_1 + \frac{m_b}{M}\mathbf{t}^{\mathrm{n}} + \mathbf{X}, \quad i = 1, 2, \ldots, Z_a\\ \mathbf{x}_i &= \mathbf{t}'_2 - \frac{m_a}{M}\mathbf{t}^{\mathrm{n}} + \mathbf{X}, \quad i = Z_a + 1, \ldots, N\end{aligned}$$

If i and j are in different clusters then

$$(\mathbf{x}_i - \mathbf{x}_j) = \left(\mathbf{t}'_i - \mathbf{t}'_j \pm \mathbf{t}^{\mathrm{n}}\right)$$

so that the inter-electronic part of the potential has a dependence upon the translationally invariant nuclear coordinates. The coordinates of the electron-nucleus attraction terms take the form:

$$(\mathbf{x}_i - \mathbf{x}_a) = (\mathbf{t}'_i), \quad (\mathbf{x}_i - \mathbf{x}_b) = (\mathbf{t}'_i + \mathbf{t}^{\mathrm{n}})$$

if i is in the first cluster and

$$(\mathbf{x}_i - \mathbf{x}_b) = (\mathbf{t}'_i), \quad (\mathbf{x}_i - \mathbf{x}_a) = (\mathbf{t}'_i - \mathbf{t}^{\mathrm{n}}) \tag{48}$$

if i is in the second cluster. It is easily seen that this choice does allow the dissociation into a pair of separate atoms but at the cost of making the electronic repulsion term dependent upon what is formally, a nuclear variable and also of considerably complicating the description of the permutational symmetry of the electrons. Again, clamping the nuclei would not avoid this difficulty. It would simply make $\mathbf{t}^n$ a constant. Thus with this choice it would *not* be possible to match the electronic part of the Hamiltonian found here to the usual clamped nuclei electronic Hamiltonian.

The two sets (45) and (48) of translationally invariant coordinates are related by

$$\begin{aligned}\mathbf{t}'_i &= \mathbf{t}_i - \frac{1}{2}\mathbf{t}^{\mathrm{n}}, \quad i = 1, 2, \ldots, Z_b\\ \mathbf{t}'_i &= \mathbf{t}_i + \frac{1}{2}\mathbf{t}^{\mathrm{n}}, \quad i = Z_b + 1, \ldots, N\end{aligned} \tag{49}$$

and obviously, any wave function obtained in one set of coordinates can be re-expressed, though perhaps not at all conveniently, in the other. This establishes that the exact solutions to the problem expressed in either set of coordinates yield the same energies, provided that the same boundary conditions are imposed, in spite of having different looking wave functions. There is therefore, absolutely nothing faulty in the mid-point choice of origin. If exact solutions to the problem were available with this coordinate choice, among them would be the almost-separated atom ones, it is just that their formulation would involve a complicated mixture of electronic and nuclear coordinates and thus they would not easily be approximated by trial functions in product form.

Although our discussion has been limited to the diatomic, the results can be generalized. If in a polynuclear system, the electronic origin is taken at the centre of nuclear mass, it can be shown [11] that it is always possible to write an FFE Hamiltonian like (42) and that the interparticle distances can be mapped onto those in the ordinary clamped nuclei Hamiltonian, just as in the centre-of-mass choice for the diatomic. But the behaviour of the coordinates at large internuclear distances exhibits the same problems as in the diatomic. Choices of electronic coordinates to get round these problems, while preserving the form of the kinetic energy terms in the FFE, make a similar mapping of the potential terms, impossible.

This discussion shows is that it is not possible to write a translationally invariant Hamiltonian in terms of a set of coordinates which are settled so as to distinguish between electronic and nuclear variables and which also allow its asymptotic behaviour to be physically plausible. This would still be the case if the nuclei were distinguishable, so that nuclear permutations need not be considered.

4 The spatial part of the wavefunction

Whatever the precise choices made for the electronic coordinates it is natural to look for a solution to the spatial part of the problem in terms of an expansion of products of the form

$$\psi^J_{pm}(R, \mathbf{r}) = \overline{\chi}^J_{pm}(R, \mathbf{r})\eta^J_{ps}(R) \tag{50}$$

where R can be treated as a a parameter in the construction of $\overline{\chi}^J_{pm}$ and then be treated as a variable in the construction of

η^J_{ps}. So p may be regarded as part-specifying the electronic state of the problem while m must also appear in the electronic part of the solution because the electrons must carry the z-component of the angular momentum to complete the electronic state specification. The subscript s on η^J_{ps} allows for "vibrational" states within a given electronic state.

Before attempting to specify coordinate choices more closely consider the construction of the matrix elements (38), (40) and (41) using product functions (50), generalizing somewhat the pioneering discussion of Kołos [12]. This will be done in two stages, as usual, first integrating over the electronic variables to give an effective Hamiltonian in terms of the nuclear variable R.

$$\begin{aligned}
&\mathsf{H}_{p'm,pm} \rightarrow \mathsf{H}^{\mathrm{nuc}}_{p'm,pm} = \\
&-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\langle\overline{\chi}^J_{p'm}|\nabla^2(\mathbf{r}_i)|\overline{\chi}^J_{pm}\rangle \\
&-\frac{\hbar^2}{2}\sum_{i,j=1}^{N}\frac{1}{\overline{\mu}_{ij}}\langle\overline{\chi}^J_{p'm}|\vec{\nabla}(\mathbf{r}_i)\cdot\vec{\nabla}(\mathbf{r}_j)|\overline{\chi}^J_{pm}\rangle \\
&+\langle\overline{\chi}^J_{p'm}|\mathsf{V}(R,\mathbf{r})|\overline{\chi}^J_{pm}\rangle \\
&+\frac{\hbar^2(J(J+1)-m(m+1))}{2\mu_{ab}R^2} \\
&\langle\overline{\chi}^J_{p'm}|\overline{\chi}^J_{pm}\rangle + \frac{1}{2\mu_{ab}R^2}\langle\overline{\chi}^J_{p'm}|\mathsf{l}^+\mathsf{l}^-|\overline{\chi}^J_{pm}\rangle \\
&-\frac{\hbar^2}{2\mu_{ab}}\left\langle\overline{\chi}^J_{p'm}|\overline{\chi}^J_{pm}\right\rangle\left(\frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}\right) \\
&+\frac{\hbar}{i}\left\langle\overline{\chi}^J_{p'm}|\mathsf{v}_z|\left(\frac{\partial}{\partial R}\overline{\chi}^J_{pm}\right)\right\rangle + \frac{\hbar}{i}\langle\overline{\chi}^J_{p'm}|\mathsf{v}_z|\overline{\chi}^J_{pm}\rangle\frac{\partial}{\partial R} \\
&+\frac{1}{2iR}\langle\overline{\chi}^J_{p'm}|(\mathsf{v}^+\mathsf{l}^- - \mathsf{v}^-\mathsf{l}^+)|\overline{\chi}^J_{pm}\rangle \\
&-\frac{\hbar^2}{2\mu_{ab}}\left(\left\langle\overline{\chi}^J_{p'm}|\left(\frac{\partial^2}{\partial R^2}\overline{\chi}^J_{pm}\right)\right\rangle\right. \\
&\left.+2\left\langle\overline{\chi}^J_{p'm}|\left(\frac{\partial}{\partial R}\overline{\chi}^J_{pm}\right)\right\rangle\left(\frac{1}{R}+\frac{\partial}{\partial R}\right)\right) \qquad (51)
\end{aligned}$$

while

$$\begin{aligned}
&\mathsf{H}_{p'm+1,pm} \rightarrow \mathsf{H}^{\mathrm{nuc}}_{p'm+1,pm} \\
&= -c^+_{Jm}\left\langle\overline{\chi}^J_{p'm+1}|\left(\frac{\hbar}{2\mu_{ab}R^2}\mathsf{l}^+ + \frac{\hbar}{2iR}\mathsf{v}^+\right)\overline{\chi}^J_{pm}\right\rangle \qquad (52) \\
&\mathsf{H}_{p'm-1,pm} \rightarrow \mathsf{H}^{\mathrm{nuc}}_{p'm-1,pm} \\
&= -c^-_{Jm}\left\langle\overline{\chi}^J_{p'm-1}|\left(\frac{\hbar}{2\mu_{ab}R^2}\mathsf{l}^- - \frac{\hbar}{2iR}\mathsf{v}^-\right)\overline{\chi}^J_{pm}\right\rangle \qquad (53)
\end{aligned}$$

where the implied integrations are over the electronic coordinates only. To elucidate more fully what is involved in this integration the construction of the electronic wavefunctions must be considered.

4.1 The electronic Hamiltonian

In the usual treatment of the electronic states of a diatomic molecule (see Chapter 11 [13]) is taken as one with cylindrical symmetry and the full spherical symmetry of the problem is ignored. In this restricted formulation the states with $m = 0$ are not degenerate while states with $m = \pm|m|$ form doubly degenerate pairs. Clearly $m = 1$ states are possible only if $J \geq 1$ and so on, but the role of J is not usually emphasized. In a full approach, for any given J the $2J + 1$ possible states specified by m can form a non-degenerate set.

Consider the FFE Hamiltonian: in rectangular Cartesian coordinates $\mathbf{r}_i$ has components x_i, y_i and z_i where the $z-$ axis lies along the internuclear axis which is oriented from b to a. Since $|\mathbf{C}|$ is positive, the coordinate system is a right-handed one if the original choice was a right handed one. Cartesians are the natural coordinate choice for performing clamped-nuclei calculations but they are difficult to use in the present context for it is not easy to construct eigenfunctions of l_z in terms of them. If $\mathbf{r}_i$ is realized in spherical polars r_i, θ_i and ϕ_i then

$$\mathsf{l}_z(j) = \frac{\hbar}{i}\frac{\partial}{\partial\phi_j} \qquad (54)$$

and so the electronic wavefunction with m as the $z-$ component of angular momentum can be written as

$$\overline{\chi}^J_{pm}(R,\mathbf{r}) = \mathcal{P}[\chi^J_{pm}(R,r,\theta,\epsilon)\exp(im\phi)],\ \phi = \frac{1}{N}\sum_{j=1}^{N}\phi_j \qquad (55)$$

where r and θ (without subscripts) denote the variables collectively and ϵ denotes the variables $\epsilon_i = \phi_i - \phi_{i+1}$ with $i = 1, 2, \ldots, N-1$ collectively. $\mathcal{P}$ denotes the symmetric group projection operator that produces a spatial function of the correct permutational symmetry for the chosen electron spin eigenfunction. The volume element for integration is

$$d\mathbf{r} = \prod_{j=1}^{N} r_j^2 \sin\theta_j dr_j d\theta_j d\phi \prod_{j=1}^{N-1} d\epsilon_j$$

It is possible to eliminate r_i and θ_i in the electronic function in favour of other coordinates. The so-called "elliptical coordinate" system (properly called *prolate spheroidal*) is the most widely used choice in accurate electronic structure calculations within the clamped nuclei approximation, and is used in [14]. In this set, however, the interparticle distance (here R) is a parameter that defines the coordinate system and *not* a variable so some care must be taken if such a coordinate system is used, as it was [7]. It would however be easy to change to cylindrical coordinates as used by Hilico et al. [15] because the choice

$$z = r\cos\theta, \quad \rho = r\sin\theta \qquad (56)$$

can be made. But these choices all yield a common form in the second derivative term involving the ϕ_i in the kinetic energy operator, namely

$$\sum_{i,j=1}^{N} f_{ij}\frac{\partial^2}{\partial\phi_i\partial\phi_j}$$

in which the multiplicative operator $f_{i,j}$ does not involve the coordinates ϕ_i. Thus in the case of the choice of spherical polars

$$f_{ij}=-\left(\delta_{i,j}\frac{\hbar^2}{2m}+\frac{\hbar^2}{2\overline{\mu}_{ij}}\right)\frac{1}{r_i r_j\sin\theta_i\sin\theta_j}.$$

It is then easy to see that this part of the kinetic energy operator operating on the trial function defined in (55) results in the term

$$-\left(\frac{m}{N}\right)^2\sum_{i,j=1}^{N} f_{ij}\overline{\chi}^J_{pm}(R,\mathbf{r})$$

and that the electronic energy at any fixed value of R will be non-degenerate if $m=0$ but otherwise will be doubly degenerate just as if the problem had cylindrical symmetry.

Once again it should be stressed that it is not the coordinate choice for the Hamiltonian that matters, the fundamental properties of the Hamiltonian are quite independent of any proper coordinate choice, it is the ability to construct an appropriate trial function in terms of a particular choice of coordinates. So provided that an eigen-function of l_z is chosen as a trial function, the electronic Hamiltonian can be formulated in rectangular Cartesian coordinates if that is most convenient for computational purposes.

If the internuclear midpoint is chosen as the electronic origin and if R is chosen to be constant R_e, then the standard clamped-nuclei form for the potentials can be recovered by treating the electron-nucleus separation coordinates (46) as if the nuclei were placed symmetrically along the $z-$axis at $\pm R_e/2$. If atomic orbitals are centered on the nuclei and they are expressed in local spherical polar coordinates with azimuthal angular part

$$e^{is\phi_{ai}} \quad \text{and} \quad e^{is\phi_{bi}}$$

then it is easy to show that any linear combination of such atomic orbitals is an eigenfunction of $\mathsf{l}_z(i)$ just as long as the quantum number s is the same on each centre. So it would be perfectly legitimate to perform standard LCAO-MO calculations using the ordinary clamped nucleus approximation to obtain trial electronic wave functions with this choice of electronic origin. If would also be legitimate to do clamped nuclei calculations with any other proper choice of electronic origin but the clamped nuclei electronic Hamiltonian with such choices could not be mapped onto the ordinary clamped nuclei electronic Hamiltonian.

4.2 Electronic correction terms

Consider (51) for the case $p'=p$, $m'=m$, take the electronic wave functions to be normalised to unity and treat the terms involving the velocity operator and derivatives of the electronic wave function with respect to R as a remainder operator $\mathsf{E}^{\text{rem}}_{pm}(R)$. The expression is then:

$$\begin{aligned}
&-\frac{\hbar^2}{2\overline{m}}\sum_{i=1}^{N}\langle\overline{\chi}^J_{pm}|\nabla^2(\mathbf{r}_i)|\overline{\chi}^J_{pm}\rangle+\langle\overline{\chi}^J_{pm}|\mathsf{V}(R,\mathbf{r})|\overline{\chi}^J_{pm}\rangle\\
&\quad-\frac{\hbar^2}{2}\sum_{i\neq j=1}^{N}\frac{1}{\overline{\mu}_{ij}}\langle\overline{\chi}^J_{pm}|\vec{\nabla}(\mathbf{r}_i)\cdot\vec{\nabla}(\mathbf{r}_j)|\overline{\chi}^J_{pm}\rangle\\
&\quad+\frac{1}{2\mu_{ab}R^2}\langle\overline{\chi}^J_{pm}|\mathsf{l}^+\mathsf{l}^-|\overline{\chi}^J_{pm}\rangle\\
&\quad+\frac{\hbar^2(J(J+1)-m(m+1))}{2\mu_{ab}R^2}-\frac{\hbar^2}{2\mu_{ab}}\left[\left(\frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}\right)\right]\\
&\quad+\mathsf{E}^{\text{rem}}_{pm}(R)
\end{aligned}\tag{57}$$

with

$$\frac{1}{\overline{m}}=\frac{1}{m}+\frac{1}{\overline{\mu}_{ii}}$$

For calculations at a fixed value of R, evaluating the first two terms yields a quantity $E^{\text{ffn}}_{pm}(R)$ which will be just the sum of an electronic and a classical nuclear repulsion energy for electrons of mass $\overline{m}$. In standard calculations this is regarded as a point on the clamped nuclei potential curve for nuclear motion. The classical nuclear repulsion energy plays no part in determining the trial wavefunction nor the electronic energy of the system. It simply provides an energy origin. This energy origin increases with out limit as R tends to 0 but the wave function for the system will tend to a wavefunction for the united atom and the electronic energy towards that for the united atom too. Of course the state of the united atom that is approached will depend on the molecular state itself. As R increases without limit so the inter-nuclear repulsion will vanish and the trial wavefunction will approach that for two separate electronic entities each based on a particular nucleus. In general one might expect the state of lowest energy to be that described by two separated atoms but the separated entities would have to be such that their total angular momentum would be J as defined by the molecular system and the systems jointly would have to have a totally antisymmetric electronic wavefunction.

Assuming that the function $\overline{\chi}^J_{pm}$ has been determined as a good approximation at a point to a solution of the FFE Hamiltonian, using it to construct an expectation value of the next two terms will yield $E^{\text{dc}}_{pm}(R)$ which will provide a "correction" to the potential analogous to the so-called "diagonal Born–Oppenheimer" (DBOC) correction [16] in standard calculations. The expected value of the first term should change perfectly smoothly between $R=0$ and $R\to\infty$ but the second term is problematic as $R \to 0$. Suppose that the electronic trial function is chosen to be an angular momentum eigenfunction with value $j \geq m$ then the expected value of the second term is

$$\frac{\hbar^2}{2\mu_{ab}R^2}(j(j+1) - m(m-1))$$

However, as $R \to 0$ and the trial function approaches that of the united atom so it gets closer to being an angular momentum eigenfunction for the united atom and, calling this j, then unless $j = 0$ or $j = m - 1$, this term is divergent. This divergence is not a physical one, it arises simply because of the way that the problem has been split up and it may prevent the use of this term as a correction when R becomes small. The term should vanish as R becomes large.

It is not clear to what extent these observations should generalize to a polynuclear molecule because in the polynuclear case there would be no explicit dependence on the angular momentum in the electronic wavefunction, as there are no explicit angular momentum terms in the FFE Hamiltonian and there will be no explicit coupling of the kind that occurs in the diatomic via the m value.

The next two terms specify nuclear motion, the first of them with an angular momentum dependent modification of the potential, and can be used to construct approximate nuclear motion functions $\eta^J_{ps}(R)$ with the calculated potential. There will be analogous terms in the polynuclear case [11]. The rotational part will reflect the general asymmetric top form of a polynuclear system and the kinetic energy part will involve all $3A - 6$ internal coordinates.

The remainder term can then be estimated to first order by calculating the expected value of $\mathsf{E}^{\text{rem}}_{pm}(R)$ with the trial function so obtained. For a homonuclear diatomic with the electronic origin chosen at the nuclear midpoint the velocity operator vanishes and it might be hoped that this operator was anyway of small effect. It should be noticed that the remainder term does give rise to an extra kinetic energy operator which could be of significant effect were the electronic "overlap" term by which it is multiplied, to be large. Again analogous terms arise in the polynuclear system.

The terms (52) and (53), which can arise even when $p = p'$, will couple the various m states that have electronic parts determined as solution of the FFE Hamiltonian.

Thus, provided that one uses a suitable coordinate system and does not attempt to consider states in which R becomes very small it would seem perfectly possible to perform well defined calculations on the diatomic molecule by separating the nuclear and electronic motions. However, it is not possible simply to treat a potential $E^{cn}(R)$ obtained from a solution of the problem specified by the standard clamped nucleus Hamiltonian (4), as if it were $E^{ffn}(R)$ as arising from the first two terms of (57). For a given nuclear geometry, the Hamiltonian (42) has the same spectrum as that of (4) only if the nuclear masses are treated as increasing without limit. It is not therefore, in general, possible to treat the electronic wave functions and energies arising from (4) as part solutions to the problem as specified by the full Hamiltonian. However, since the electronic mass may be treated as a scale factor in finding solutions to (4), the resulting wave functions may be scaled to a correspond to a mass value appropriate to the problem as specified by a particular internal coordinate choice. These scaled functions can then be used as trial functions to compute $E^{ffn}(R)$ and $E^{dc}(R)$ as defined by the Hamiltonian with this coordinate choice. Thus although it is not possible to specify uniquely to which question the standard clamped nucleus Hamiltonian (4) is the answer, it is possible to use it properly in the context of a fully specified internal motion Hamiltonian.

5 Conclusions

Even in the case of diatomic molecules there is clearly still a need for careful computational work to yield results to compare with the increasingly accurate experimental work on molecular spectra. Although the contributions of Serafin Fraga to the field were not in this area, I remember stimulating discussions with him of interesting problems in other areas of quantum chemistry. I hope that he would have been stimulated by the discussion that I have offered here in his memory.

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