

Treating nuclei in molecules with quantum mechanical respect.

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June 23, 2016

1 Introduction

In 1929 Dirac wrote famously [1]

The fundamental laws necessary for the mathematical treatment of large parts of physics and the whole of chemistry are thus fully known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.

It is worth reminding ourselves of the context of this remark. In the text immediately prior to the famous quotation, Dirac had identified the exact fitting in of quantum mechanics with relativity ideas as the remaining imperfection in fundamental physical theory. For the consideration of atomic and molecular structure and ordinary chemical reactions he thought it would usually be sufficiently accurate to neglect the relativity variation of mass with velocity, and assume only Coulomb forces between the various electrons and atomic nuclei. A molecule considered as a quantum mechanical collection of electrons and nuclei is customarily described by the usual Coulomb Hamiltonian H acting on an Euclidean configuration space defined by the particle coordinates with Schrödinger equation

$$H\Phi = E\Phi. \quad (1)$$

More explicitly, for a system of N_e electrons and N_n atomic nuclei we have

$$\begin{aligned} H = & \sum_{g=1}^{N_n} \frac{\mathbf{p}_g^2}{2m_g} + \frac{e^2}{8\pi\epsilon_o} \sum_{g,h=1}^{N_n} \prime \frac{Z_g Z_h}{r_{gh}^{nn}} \\ & + \sum_{i=1}^{N_e} \left(\frac{\mathbf{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_o} \sum_{g=1}^{N_n} \frac{Z_g}{r_{ig}^{en}} \right) + \frac{e^2}{8\pi\epsilon_o} \sum_{g,h=1}^{N_n} \prime \frac{1}{r_{gh}^{nn}}. \end{aligned} \quad (2)$$

The configuration space is $\mathbb{R}^{3N_n+3N_e}$, where \mathbb{R} denotes the set of real numbers. The interparticle distances are: $r_{gh}^{nn} = |\mathbf{x}_g^n - \mathbf{x}_h^n|$, $r_{ig}^{en} = |\mathbf{x}_i^e - \mathbf{x}_g^n|$, and $r_{ij}^{ee} = |\mathbf{x}_i^e - \mathbf{x}_j^e|$ in terms of particle coordinates $\{\mathbf{x}_i^e, \mathbf{x}_g^n\}$ in a laboratory frame. Here and elsewhere we use (i, j) and (g, h) as indices for electrons and nuclei respectively. The primes on the summation symbols mean that terms with identical indices ('self-interactions') are to be omitted.

The Hamiltonian is only Galilei and not Lorentz invariant but the Coulomb form of the interaction is legitimate in the absence of external electromagnetic fields.

In computational quantum chemistry it is usual simply to assert that "making the Born-Oppenheimer (BO) approximation" the Hamiltonian of interest for electronic structure calculations is

$$\begin{aligned} H^{conv} = & \sum_{g=1}^{N_n} \frac{\mathbf{p}_g^2}{2m_g} + \frac{e^2}{8\pi\epsilon_o} \sum_{g,h=1}^{N_n} \prime \frac{Z_g Z_h}{r_{gh}^{nn}} \\ & - \frac{e^2}{4\pi\epsilon_o} \sum_{g=1}^{N_n} \frac{Z_g}{r_{ig}^{en}} + \frac{e^2}{8\pi\epsilon_o} \sum_{g,h=1}^{N_n} \prime \frac{1}{r_{gh}^{nn}}. \end{aligned} \quad (3)$$

The nuclear positions are treated as constant vectors \mathbf{a}_g so that the Coulomb energy of the nuclei, V_{enn} , is a pure number and the r_{ig} , though dependent on the \mathbf{a}_g , are functions of the electronic variables only. Thus (3) arises from (2) by allowing the nuclear masses to increase

without limit *and* then choosing particular values for the nuclear position vectors. Of course nuclear motion has to be restored if the description is to account for vibrations and rotations, chemical reactions and so on. The trial wavefunctions are thus of product form, one part arising from the solution of the electronic problem with the nuclear variables as parameters and the other part as a function of the nuclear variables. The eigenvalues found by a calculation at a particular value of the nuclear variables are called *electronic energies* and when added to the nuclear repulsion calculated classically are said to be a point on a *potential energy surface* (PES). The PES is defined only for distinct nuclear geometries. It is independent of uniform translations and rigid rotations of the nuclear positions.

The theory conventionally invoked to tie these two Hamiltonians together is either that of Born and Oppenheimer [2], or of Born as presented in the book by Born and Huang [3]. It is generally assumed that the latter theory includes the former as a special case although there does not seem to be an explicit demonstration of this in the literature. It is also generally assumed that if the Born and Huang approach were carried through fully, then an exact result could be obtained. The form (3) will be referred to as the *clamped nuclei* Hamiltonian.

There can be no doubt that computational work undertaken starting with (3) has proved extremely successful and a computation with it is often regarded as a sort of “instrument” used to reveal new chemical information. There can be no doubt about its utility and it can thus be regarded as a self-justifying scheme. However the scheme itself is also regarded as tying the traditional theories of chemistry, involving bonds and molecular structures and the like, to quantum mechanics, and hence “justifying” the tradition. The central element in this fitting is the identification of the nuclei, even when quantum mechanically, they are indistinguishable particles. Without identifying nuclei, molecules cannot be identified and hence no relevant theory could be developed. If one is going to start with the full Hamiltonian and treat the nuclei properly, whatever is done will not attract any interest from chemists unless it can yield the kind of results that can be considered as “just like” those obtained from the the clamped nuclei Hamiltonian (3). It is appropriate then to consider the nature of the full Hamiltonian rather more.

2 The nature of the full Hamiltonian.

As a start it is useful to recapitulate some mathematical results relevant to the present discussion. It would perhaps prove tedious to reference the origins of such results but, if required, a relevant selection placed in an appropriate context can be found in Sutcliffe [4].

The full Hamiltonian (2) is not only Hermitian but self-adjoint too. Providing the continuous spectrum arising from uniform translational motion is removed, it has a spectrum which can consist of two parts, a discrete part and an essential part. It need not have a discrete part but if it has, it ends where the essential spectrum begins which is at the energy of the lowest two-body decomposition possible. The discrete states correspond to bound states and have square-integrable wavefunctions. It is however possible that members of the pure point spectrum (which includes the discrete spectrum) occur in the essential spectrum, which otherwise consists of entirely continuous functions. To exemplify this, the discrete spectrum of the hydrogen atom ends at the first ionisation energy and the essential spectrum consists of all the scattered electron states. The discrete spectrum of the helium atom again ends at the first ionisation energy but the essential spectrum here contains not only of the scattered electron states but also pure point states (resonances) from the discrete spectrum of helium-plus.

It has not yet proved possible to say anything particularly helpful about the extent of the discrete spectrum of the Hamiltonian in the multi-nuclear case, but the Hamiltonian corresponding to a neutral or positively charged atom, has a countably infinite number of discrete states. In the negatively charged atom case, at most a finite number of discrete states are possible. Unsurprisingly, this result carries over to the clamped nuclei Hamiltonian but the nature of the discrete spectrum here, depends on the nuclear geometry. The essential spectrum again begins at the first ionisation energy, but that depends on the nuclear geometry too.

The bound state eigenfunctions of the full Hamiltonian though continuous at, are not differentiable at points corresponding to particle collisions. A discussion of the consequences of this for the consideration of nuclear motion can be found in Jecko *et al*[5].

The full Hamiltonian (2) is invariant under all uniform translations and rotation-reflections and under any permutation of identical particles. Removing the translation invariance leaves the discrete states, if any, as providing a basis for irreducible representations of the orthogonal group and of the symmetric groups of the sets of identical particles. The actual representations possible of the symmetric groups are restricted by the Pauli principle depending on whether the particles are fermions or bosons.

As it stands (2) has no discrete spectrum and the translational motion must be dealt with to allow the discrete spectrum to emerge. A full discussion of these and related matters can be found

in [6] but a brief unsourced summary will be made here. Since the translation group is Abelian, it is perfectly possible to transform the laboratory coordinates to a set on $N - 1$ translationally invariant coordinates and a centre-of-mass coordinate. This transformation is a linear one and the resulting space is a coordinate space. If it is wished to retain the distinction between electronic and nuclear coordinates coupled in the Hamiltonian only by a potential term then the simplest choice is to make the electronic origin the centre-of-nuclear mass leaving one with a Hamiltonian for N_e electrons and $N_n - 1$ nuclear pseudo-particles. A nuclear permutation now involves a linear transformation of these coordinates. If one wants to keep the original coordinates, the centre-of-mass coordinate can be back-transformed and the resulting form subtracted from (2) to give a translationally invariant form. If one doesn't care about having a square-integrable wave function then one can use *coherent state functions* as trial-functions for solutions of the full problem. This approach is used by George Hagedorn [7] in his consideration of the BO approximation but it seems unlikely to commend itself to Computational Chemists.

To deal with the the invariance under the operations of the orthogonal group $O(3)$ one can transform the translationally invariant coordinates to a set of orthogonally invariant internal coordinates and three angles. Such a transformation does not yield a coordinate space but a manifold which is coordinatisable only in regions in which the Jacobian for the transformation does not vanish. No one choice of such coordinates can cover the whole space To keep the electronic coordinates in their usual form, the transformation must be specified in terms that involve the $N_n - 1$ nuclear variables to yield $3N_n - 6$ internal coordinates q_k and N_e Cartesian electronic variables \mathbf{z}_i . This is impossible with two nuclei and gives a very special result for three nuclei and is quite special for four nuclei. In general a nuclear permutation transforms the internal coordinates among themselves, though not necessarily linearly but transforms the angular coordinates into a combination of themselves and the internal coordinates. The transformation also couples the electronic angular momentum to to the nuclear motion spoiling the multiplicative form of the operator connection.

The angular eigenfunctions can be explicitly constructed and are labelled by four integers J, M, k and r . J labels the irreducible representation of $SO(3)$ while the $2J + 1$ values of M label the degenerate members of the representation. The $2J + 1$ values of k label non-degenerate eigenstates of the z component of the internal angular momentum. r takes two values and labels the parity of the state. It should be noted that the requirements of the Pauli principle upon the nuclear permutations may conflict with the description of a particular rotational state and so some states may be permutationally impossible. They may also force a particular parity on a state.

It is obvious that, strictly speaking, if one wants to get to a PES one should consider it as arising from the Hamiltonian after dealing with translation and rotational motion. To obtain an effective local nuclear motion Hamiltonian, depending only on the \mathbf{q} , can be obtained by letting the Hamiltonian operator operate on functions of product form and multiplying the resulting expression from the left by $\psi_{p'}(\mathbf{q}, \mathbf{z})$ and integrating over the \mathbf{z} . Doing this yields an equation with coupling between different electronic states, labelled by p . The effective internal motion operator is then:

$$\begin{aligned}
& \langle JMk'p' | H' | JMkp \rangle_{\mathbf{z}} = \\
& \frac{\hbar^2}{4} (b_{+2} C_{Jk+1}^+ C_{Jk}^+ \delta_{k'k+2} + b_{-2} C_{Jk-1}^- C_{Jk}^- \delta_{k'k-2}) \delta_{p'p} \\
& + \frac{\hbar^2}{4} (C_{Jk}^+ (b_{+1}(2k+1) + \lambda_+) \delta_{k'k+1} + C_{Jk}^- (b_{-1}(2k-1) + \lambda_-) \delta_{k'k-1}) \delta_{p'p} \\
& \quad + \frac{\hbar^2}{4} (C_{Jk}^+ \gamma_{p'p}^+(\mathbf{q}) \delta_{k'k+1} + C_{Jk}^- \gamma_{p'p}^-(\mathbf{q}) \delta_{k'k-1}) \\
& + \frac{\hbar^2}{2} ((J(J+1) - k^2)b + b_0 k^2 + \lambda_0 k) \delta_{k'k} \delta_{p'p} + \frac{\hbar^2}{2} \delta_{k'k} k \gamma_{p'p}^0(\mathbf{q}) \\
& + \delta_{p'p} \delta_{k'k} (K_A + E_p(\mathbf{q}) + V^n(\mathbf{q})) + \delta_{k'k} \gamma_{p'p}(\mathbf{q})
\end{aligned} \tag{4}$$

The definitions of the terms can be found in [6] but it is sufficient here to note that K_A represents the vibrational kinetic energy operator, E_p the electronic energy, V^n the nuclear repulsion operator and the terms b and b_0 are elements of a matrix closely related to the inverse of the instantaneous inertia operator matrix. It should also be noted that the γ terms arise from the interaction of the rotational with the electronic motion and tend to couple electronic states, even those diagonal in k .

If it were the case that a single electronic state dominated in the energy range of interest and that within that state for a given J only a single value of k dominated then, to a first approximation the Hamiltonian

$$(K_A + E_p(\mathbf{q}) + V^n(\mathbf{q}))$$

would determine the vibrational motion and, since the b and b_0 values are simply multipliers, the Hamiltonian

$$\frac{\hbar^2}{2}((J(J+1) - k^2)b + b_0k^2)$$

would determine the rotational motion if any contribution from λ_0 can be ignored. This separation forms the basis for the standard description of vibration-rotation motion in which the vibrational levels are treated as primary levels having rotational sub-levels. In the standard description of an oblate symmetric-top, for example, the expression becomes

$$hc(BJ(J+1) + (C - B)k^2)$$

where B and C are the rotational constants expressed in cm^{-1} .

It is argued in [8], however, that it would be logical to regard this second term as a modification to the potential in the context of solving the full rotation-vibration problem for there is no particular indication that the second term is separable. Indeed this is exactly what is done in the most accurate clamped-nuclei calculations on the Hydrogen molecule. In [9] it is shown that for the hydrogen molecule dissociating into two hydrogen atoms in their ground states, the $J = 0$ state supports 14 vibrational states, the state $J = 15$, supports 10 and for $J = 31$, only 1. In fact there are just 301 states that can be associated with the lowest electronic state of the hydrogen molecule. So it is clear that here the number of vibrational states possible is strongly associated with the rotational state. Furthermore the energy levels are inter-twined. Thus, for example, in the ground vibrational state, the rotational state with $J = 9$ has a higher energy than the $J = 0$ state has in the second vibrational state. This approach to the potential has also been used in some calculations on H_3^+ . In the case of $J = 0$ in the chosen formulation it is estimated that there are 1280 vibrational states below dissociation [10]. It seems that 46 is the highest value of J for which at least one vibrational state exists [11] but these figures should be taken as indicative rather than definitive.

The reason why one is interested in a solution of the full problem in this tricky form is because it is the form in which molecular vibration-rotation spectra are discussed in work arising from the clamped nuclei approximation. For a given rotational state J it is the eigenstates labelled by the integer k that are relevant. Indeed, their very designation as *symmetric-top* eigenfunctions makes their relevance clear.

A general back-transformation from these coordinates to the translationally invariant set is not possible and only a local, usually non-linear, transformation can be made, so it is not possible to re-write the fully invariant Hamiltonian in terms of the translationally invariant coordinate set and hence in terms of the initial set in any general way. So either one faces up to dealing with a manifold and not a coordinate space or one tries to find another way of moving directly from the translationally invariant space. Of course the orthogonal symmetry can be considered in another way by the construction angular momentum eigenfunctions as trial functions in the translationally invariant space and trying to sort from among functions with a given J a set that can be associated with the k values and parity states anticipated in the tricky approach. The J eigenfunctions could be constructed in a way analogous to way used for atoms given that individual angular momentum labels could be provided for functions of the individual translationally invariant nuclear coordinates. An approach of this kind was set out by Varga [12] *et al.*.

Of course if exact discrete solutions of (2) were known then all the symmetry requirements would be automatically enforced. The only trouble would be selecting the functions which satisfy the Pauli principle from among the set. But much more usefully it may be observed that if results can be obtained from full Hamiltonian using any decently defined square-integrable set of functions, then these results will certainly remain true for functions of the proper symmetry if the functions of the proper symmetry can be expressed in terms of the chosen set.

If it is hoped to make a connection between the results obtained using the full Hamiltonian and those obtained using the clamped nuclei Hamiltonian it is necessary to consider the extent to which such solutions might be written as a product of an electronic and a nuclear part.

3 The wave function in product form

The earliest attempt to write an exact wavefunction of the Coulomb Hamiltonian for a neutral system of electrons and nuclei in a factorised form was made by Hunter[13]. He worked directly in terms of the laboratory coordinates and simply assumed that a discrete state solution existed. For the purpose of an exposition of his argument the electronic variables will be denoted \mathbf{r} and the nuclear ones \mathbf{R} . His analysis was made in terms of conditional and marginal probability amplitudes; the wavefunction $\Phi(\mathbf{r}, \mathbf{R})$, assumed normalised, is written in the product form

$$\Phi(\mathbf{r}, \mathbf{R}) = f(\mathbf{R})\phi(\mathbf{r}, \mathbf{R}) \tag{5}$$

with the nuclear function $f(\mathbf{R})$ defined as a marginal by means of

$$|f(\mathbf{R})|^2 = \int \Phi(\mathbf{r}, \mathbf{R})^* \Phi(\mathbf{r}, \mathbf{R}) \, d\mathbf{r}. \quad (6)$$

This fixes $f(\mathbf{R})$ to within a phase factor,

$$e^{i\theta(\mathbf{R})} \quad (7)$$

where $\theta(\mathbf{R})$ is a real function of the nuclear coordinates. In the absence of a criterion to choose it, Hunter suggested taking simply

$$f(\mathbf{R}) = -|f(\mathbf{R})| \text{ or } f(\mathbf{R}) = |f(\mathbf{R})|. \quad (8)$$

The associated function, ϕ , is then defined to be the quotient

$$\phi(\mathbf{r}, \mathbf{R}) = \frac{\Phi(\mathbf{r}, \mathbf{R})}{f(\mathbf{R})} \quad (9)$$

and it satisfies the normalization condition

$$\int \phi(\mathbf{r}, \mathbf{R})^* \phi(\mathbf{r}, \mathbf{R}) \, d\mathbf{r} = 1$$

for all \mathbf{R} . Obviously this construction would be problematic if either $f(\mathbf{R})$ has zeroes for finite \mathbf{R} or $\Phi(\mathbf{r}, \mathbf{R})/f(\mathbf{R})$ is too irregular at infinity. The construction, if applicable, is available for any wavefunction Φ_i and so the nuclear functions $\{f(\mathbf{R})_i\}$ are required generally to be quite different from the usual approximate nuclear wavefunctions for vibrationally excited states which do have nodes [14]. Equally, it is evident that every wavefunction Φ_i has its own distinct electronic factor, ϕ_i ; this is to be contrasted with the clamped nuclei description where whole groups of approximate eigenfunctions $\{\Phi_\alpha\}$ share one electronic state φ which supports a vibration-rotation manifold of states.

Hunter goes on to develop a set of equations that are claimed capable of yielding the exact solution in product form and this line has been followed by Gross [15] and by Cederbaum [16].

4 The beginning of full wavefunction trials.

Trials that begin from the clamped nuclei Hamiltonian extended along the Born-Huang lines will not be considered further here. It should be remembered too, that there is a completely different way of developing the clamped-nuclei results, the *generator coordinate approach* that began in nuclear structure theory and was developed in a molecular structure context as reviewed in [17] but does not seem to have been used yet on other than diatomic molecules. Some work has also been done of the construction of permutationally invariant PES summarised in [18].

Full wavefunction work done in the last twenty or so years will not be explicitly mentioned for I regard that as “work in progress”. So my “history” will stop in the middle nineties. It will also exclude work on diatomics. However it seems appropriate to mention some reviews that cover some aspects of the work unmentioned here. One by Woolley and me [19], one by Nakai[20] and one by the Adamowicz group [21].

The first moving nuclei calculations were made by Thomas [22] – [27] and by Thomas and Joy [28] beginning in 1969. Here Slater functions were used in a one-centre expansion approach. I cannot speak sufficiently highly of this endeavour. I do wish that it was more widely known and regret very much that even though I read it at the time of publication I failed to grasp its full significance. The first paper in the series is slightly defective for it takes the full Hamiltonian in a form where the nitrogen nucleus is fixed as just the same as the laboratory fixed Hamiltonian with the nitrogen nucleus kinetic energy term just dropped. But that isn’t a big error. This is how the first paper begins.

Schrödinger’s time independent equation was solved approximately using the variational theorem for methane, ammonia, water, and hydrogen fluoride with the kinetic energy operators of the protons included in the Hamiltonian and the electrons and protons described by Slater orbitals. One minimal basis confirmation was used for the electrons and twelve, twenty, six, and one configurations were used for methane, ammonia, water, and hydrogen fluoride respectively. The kinetic energies of the protons were found to be about three per cent of the bond energies. The calculations yielded protonic spectra similar to the electronic spectra.

I admire it because it seems to me to lay out exactly the way one ought to proceed in these matters. Their conclusion was:

This calculation gives for the structure of the ammonia molecule one which is radically different from the usual one. The molecule appears as an inner ellipsoid of electronic charge surrounded by a belt of protonic charge. A spectrum of protonic states emerges similar to the electronic states. **The vibrational and rotational states do not appear....**

By 1970 with the aid of Hubert Joy, Thomas had got things sorted out and was using a Hamiltonian with the centre-of-mass motion separated out. The results were not too different from that obtained earlier but what is striking about the work is the conclusion that they made:

If the result of the calculations [here] described are correct it will be necessary for quantum chemistry to modify its views on molecular structure.

What they had noticed was that they still couldn't get vibrations and rotations and neither was a dipole moment possible.

The results of this pioneering work on NH_3 and CH_4 were insufficiently conclusive to prove encouraging to a wider community of workers. Nevertheless the approach was again taken up by Pettitt in 1986 [29] developing a more flexible basis set and a self-consistent field approach. They say at the end of their exposition:

From the work of Thomas it is known that minimisation of the energies of HF, H_2O , NH_3 , and CH_4 with respect to the parameters in minimal basis sets of Slater-type orbitals for both electrons and protons gives physically reasonable states with the protons localised near the bond lengths of these molecules. The picture of XH_N outlined above, in terms of mutually consistent electron and proton states realised by orbitals which are functions of their translationally invariant coordinates, shows formally how to pursue this description to the Hartree-Fock limit for both particles. It might be necessary to go beyond this limit using configuration mixing for both particles, or explicitly correlated proton wavefunctions, to obtain an accuracy comparable to other ab initio methods, in which case the method can be expanded to include the appropriate trial wavefunctions. **Aspects of molecular geometry usually summarized by bond lengths and bond angles most directly arise in this method as symmetry properties of multi-particle wavefunctions and their associated reduced density functions.** The formalism has been presented here for single-determinantal proton wavefunctions, but the basic variational approach can be extended to multi-determinantal forms and analogous symmetric wavefunctions for deuterons (spin = 1 bosons). At present, we are developing computer codes to determine the level of accuracy of electron-proton SCF wavefunctions for first- and second-row hydrides.

Some calculations were presented in the following year [30] but in these the electronic motion was somewhat modelled to avoid some integral evaluation, but I think that nothing essential was thereby missed. These are their conclusions. The authors characterised the results obtained in this last paper as :

a fair, but not quantitatively satisfactory, description of the radial motion of (the) protons.

Meanwhile development of the use of Gaussian orbitals in electronic structure calculations encouraged other approaches and in 1973 Almström [31] proposed a computational scheme for moving nuclei based on Gaussian functions. In a later paper [32] he showed how calculations might be performed on a system with total angular momentum 0 and positive parity; he illustrated the technique on HD^+ and obtained pretty accurate values for the total energy. An interesting aspect of his work is his attempt to develop coordinates that permuted into one another under permutations of identical particles. Such behaviour is vital if an orbital description is to be offered as a trial function. He developed a set of "non-adiabatic" Gaussian orbitals based upon the nuclear positions of the lowest energy obtained in a clamped-nuclei calculation. He thought that his approach might be possible for systems of up to ten particles but I can discover no more work along his lines.

In 1976 Guy Woolley [33] published an article on the relationship between quantum theory and molecular structure which led to a sometimes heated debate on whether or not molecular structure could be accommodated by molecular wavefunctions that allowed the nuclei to move. This is another case in which I failed at the time to grasp the full significance of the work, recognising only its relevance to the translational motion. The debate encouraged Essen [34] to look again at the role that the ratio of the electronic to nuclear mass might play in considering such matters; interestingly enough, he came to the conclusion that it was the form of the Coulomb interaction

and not the smallness of the electron to nuclear mass ratio that made plausible treating the nuclei as fixed. It also stimulated work by Monkhorst who, in 1987, proposed treating the moving nuclei problem by an extension of the coupled-cluster method [35] using explicitly correlated Gaussian functions, but no actual calculations appear to have been made in this way. Almost twenty years later, two papers with Frank Harris, appeared outlining a formal procedure for the calculation of the required integrals but again, nothing seems to have been done using it. I should like to recommend, most strongly, that these two papers be read by anyone interested in the full problem. They express in a vigorous and clear way precisely what the problems are, both practical and theoretical, in attempting trial solutions of the full problem. They also provide intriguing (but distinctly different) accounts of how the results of clamped-nuclei calculations might be related to calculations using the full Hamiltonian.

The next development along these lines is the publication in 1991 by Kozłowski and Adamowicz [36] of an approach to the moving nuclei problem using correlated Gaussian geminal functions somewhat like those chosen by Almström, although the inspiration of this work originated in contemporary ideas about correlated Gaussians in electronic structure calculations. Slightly later Nakai and his group [37] introduced an orbital approach to the problem in which molecular orbitals were constructed both for the nuclei and the electrons.

It is the “orbital” approach, correlated or not which, it seems to me underlies the current full Hamiltonian work and is an appropriate point for me to end my “history”.

5 Some thoughts.

I have to admit that I admire the work done by Thomas and by Pettitt because it seems to me that they tackle the problem exactly as one would tackle it if one knew about quantum mechanics and atoms but knew nothing about “molecular structure”. It is an essentially one-centre approach and it was a natural one in the case of their examples where there was a unique heavy nucleus, and the chosen orbital basis behaved in the usual way under permutation of identical particle variables. For any other choice of origin if a orbital basis of a natural kind is to be used then suitable variables must be chosen in terms of the given translationally invariant set.

The point that I wish to make is that their results are not biased by an anterior view of what a molecule ought to be. I am anxious that whatever we do with the full wavefunction calculations we don’t slip a covert molecular view into our methods and hence, bias our results. If we are to join full wavefunction results to clamped nuclei results, we must do so without cheating.

I should however like to end on a personal note. I think that the early death of Pierre Claverie was a great loss for the field. He surely would have been a huge influence on the development of full solutions.

At a completely different level I think the death late last year of Jan Boeyens is also a loss for the field. It is easy to make fun of his views but he did press hard on ordinary chemists to think about the way they thought. The last of his books (“Electronic Structure and Number Theory” no less!) ends with:

It is a myth that chemistry derives from quantum theory. More fundamental than both is the periodic table that reduces the properties of matter to a number basis, which is revealed only peripherally in the differential equations of quantum theory.

Really? Perhaps. But it makes you think.

And thinking myself enables me to express my grateful thanks to Guy Woolley and to Jonathan Tennyson for their encouragement over the last thirty years or so.

6 References

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