”What mathematicians know about the solutions of Schrodinger Coulomb Hamiltonian. Should chemists care?”

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OUTLINE

- What is known mathematically about the spectrum of the standard Schrödinger equation with just Coulomb forces acting, describing the motions of both electrons and nuclei. How the solutions may be classified according to the permutational and other symmetries of the particles involved and the division of the spectrum into discrete and essential parts.

- What happens to the spectrum when the nuclei are clamped?

- To what extent do the Born and Oppenheimer or the Born approach justify a move from the clamped nuclei solutions to the full solutions.

The Coulomb Hamiltonian for a system of N electrons and A atomic nuclei

$$\mathsf{H} = \sum_{g}^{A} \frac{\mathsf{p}_g^2}{2m_g} + \frac{e^2}{8\pi\epsilon_o} \sum_{g,h=1}^{A}{}' \frac{Z_g Z_h}{r_{gh}}$$

$$+ \sum_{i=1}^{N} \left(\frac{\mathsf{p}_i^2}{2m} - \frac{e^2}{4\pi\epsilon_o} \sum_{g=1}^{A} \frac{Z_g}{r_{ig}} \right) + \frac{e^2}{8\pi\epsilon_o} \sum_{i,j=1}^{N}{}' \frac{1}{r_{ij}}$$

In 1951 Kato established that the Coulomb Hamiltonian, H, is essentially self-adjoint. This property, which is stronger than Hermiticity, guarantees that the time evolution

$$\Psi(t) = \exp(-i\mathsf{H}t/\hbar)\Psi(0)$$

of a Schrödinger wavefunction is unitary, and so conserves probability.

The first thing that Kato did was to separate out the centre-of-mass motion from the problem in the usual way to yield a Hamiltonian H' which depends only on $3(A+N)-3$ relative coordinates $\mathfrak{t}$.

For a mathematician the specification of differential operator thus far leaves the problem vague and as Kato says, “we cannot expect such an obscure operator to be self-adjoint in the literal sense.” To remove this vagueness one must specify the domain of the operator, that is say what sort of functions it is supposed to operate on and one must specify the behaviour of the potential.

So what Kato does is to say

- H must be a symmetric (Hermitian) operator
- H can be applied on all functions of the form

$$g(\mathbf{t}) = P(\mathbf{t}) \exp(-(\sum_{i=1}^{A+N-1} r_i^2)/2)$$

where P is a polynomial and $r_i = |\mathbf{t}_i|$.

He also puts conditions on the potential and for our purposes here these conditions hold for power potentials of the form r^{-m} provided that m is positive and less than 3/2. It does NOT hold for potentials like r^{-2} and this is what makes relativistic calculations so tricky to be sure about. But the coulomb Hamiltonian is OK.

What Kato showed in Lemma 4 of his amazing paper was that for a potential so specified and for any function f in the domain $\mathcal{D}_0$ of the full kinetic energy operator T_0, the domain of full problem $\mathcal{D}_V$ contains $\mathcal{D}_0$ and there are two constants a, b such that

$$||\mathsf{V}f|| \leq a||\mathsf{T}_0 f|| + b||f||$$

and that a can be taken as small is liked. This result is often summarised by saying that the Coulomb potential is small compared to the kinetic energy.

Given this result he proved in Lemma 5 that the usual operator is indeed, for all practical purposes, self-adjoint and is bounded from below.

The smallness of the Coulomb potential can be used to establish also that H is bounded from below. The lowest eigenvalue E_0, however, lies at the *bottom of a continuum*, and so the associated eigenfunction describes a *scattering* state. However after the removal of translational motion H' is bounded from below by a negative value that need not be the bottom of a continuum.

It thus makes sense to suppose that one can get all that one wants by considering

$$\mathsf{H}'(\mathbf{t})\Psi(\mathbf{t}) = E\Psi(\mathbf{t})$$

E lies on the real line. Is it isolated or part of a continuum?

Does Ψ lies in the Hilbert space $\mathcal{L}^2$ or not?

Ψ has continuous derivatives of the second order in a region S of configuration space where $\mathsf{V}(\mathbf{r})$ is sufficiently regular.

For the case of the Coulomb potential this means that problems arise only at singular points of the potential where the derivatives result in delta functions.

Later work by Kato established the *cusp conditions* on the behaviour of Coulomb wave functions in many of the singular cases.

The spectrum $\sigma(\mathsf{A})$ of a self-adjoint operator A may be classified into *discrete* and *essential* parts. The discrete spectrum $\sigma_{\mathsf{d}}(\mathsf{A})$ is the subset of the pure point spectrum that consists of isolated eigenvalues of finite multiplicity. The essential spectrum $\sigma_{\mathsf{ess}}(\mathsf{A})$ is the complement of the discrete spectrum.

$$\sigma_{\mathsf{ess}}(\mathsf{A}) = \sigma(\mathsf{A}) \backslash \sigma_{\mathsf{d}}(\mathsf{A})$$

The discrete spectrum and the essential spectrum are, by definition, disjoint; however, although the essential spectrum is always closed, the discrete spectrum need not be.

The essential spectrum describes scattering states of the system (and, in some cases, resonances) while the discrete spectrum describes bound states.

The spectrum of the translationally invariant Hamiltonian is independent of the way in which the $\mathfrak{t}$ are chosen provided that they are linearly independent and translationally invariant.

The spectrum of H' may (but need not) have a discrete part, and the start of the essential part is established by means of so-called HVZ theorem

$\sigma_{ess}(\mathsf{H}') = [\Sigma, \infty)$ where Σ is the energy of the lowest two-body cluster decomposition of the $A+N$particle system.

The essential spectrum of the hydrogen atom begins at zero energy. It is absolutely continuous and does not contain any pure point members; it describes the scattering states of a single electron and a nucleus. The wave functions here are finite at infinity, going asymptotically like trigonometric functions dependent on a phase angle determined by the energy of the state for any given value of the radial coordinate. These functions are NOT square integrable and although they do lie in a vector space, it is not the normed Hilbert space in which the bound states lie.

For all other atoms the first ionization energy is such that the essential spectrum begins at somewhat below zero energy. It contains states describing the scattering of an electron from a singly ionized atom which is a resonance, two electrons from a doubly ionized atom, a scattering state for Helium, for example, and so on.

Does a Coulomb Hamiltonian describing a given collection of electrons and nuclei have any discrete spectrum at all before the start of the essential spectrum?

This requires the demonstration of a so-called ‘binding condition’, first obtained by Zhislin in 1961

For a collection of N electrons and A fixed nuclei with total (positive) charge Ze, the bottom of the spectrum of H′ is a genuine $N-$particle bound state that satisfies the
Schrödinger equation with some energy E_0 for each choice of the locations of the nuclei, provided $N < Z + 1$. The same result has recently been obtained when account is taken of the ever-present quantized electromagnetic field

In the single nucleus case there are infinite number of bound states if the atom is electrically positive or neutral.

If the system has an overall negative charge then it has at most a finite number of bound states.

Nyden Hill showed in 1977 that the H^- ion had only one bound state.

Given a trial wave function Φ with an expectation value $< \mathrm{H}' >$ which is below the bottom of the essential spectrum, then H' has at least one discrete negative eigenvalue.

At present the most that has been proved is that the hydrogen molecule has at least one bound state.

The variables symbols used to designate particles, simply specify field points, and cannot actually be particle coordinates because of the indistinguishability of sets of identical particles.

Only operators symmetric in all the coordinates of identical particles can properly be deployed in the calculation of expectation values that represent observables. Weyl discusses this in Section C 9 of Chapter IV of *Group Theory and Quantum Mechanics*

> Physical quantities have only an objective significance if they depend *symmetrically* on the two individuals. It is impossible for either of these individuals to retain his identity so that one of them will always be able to say "I'm Mike" and the other "I'm Ike". Even in principle one cannot demand an alibi of an electron! In this way the Leibnizian principle of *coincidentia indiscernibilium* holds in quantum mechanics.

This discussion holds for identical particles of any kind that are to be described by quantum mechanics and it precludes the specification of, for example, the expected value of a particular interparticle distance when chosen from a set describing more than two identical particles.

The requirement that an operator be totally symmetric means that the effect of an operator on a function in the sub-space of a particular permutational symmetry must be to produce another function in the sub-space. To put it slightly differently: it is easy to see that an operator which is unsymmetric in form could not possibly commute with the Hamiltonian, which is symmetric, and so could not be simultaneously definite with the energy of the system.

H$'$ is invariant under all orthogonal transformations of the translationally invariant coordinates so its eigenfunctions will provide a basis for irreducible representations (irreps) of the orthogonal group in three dimensions O(3).

The eigenfunctions are classified by their parity; each kind consists of eigenfunction sets, each with degeneracy $2J+1$, according to the irrep $J = 0, 1, 2, \ldots$ of SO(3) to which the eigenfunctions belong. The representations of O(3) are distinct for each parity.

For molecules, descriptions of rotation-reflection symmetry are usually offered in terms of three angular coordinates and a parity specification, together with $3(A+N)-6$ *internal* coordinates, which are invariant under all rotation-reflections.

It is supposed that the three orientation variables $\phi_m, m = 1, 2, 3$ are specified by means of an orthogonal matrix $\mathbf{C}$,

$$\mathbf{t} = \mathbf{C}\mathbf{z}$$

Generally internal coordinates, denoted q_i, are expressible in terms of scalar products of the $\mathbf{t}_i$ and the $\mathbf{z}_i$ must be completely expressible in terms of the q_i

There are many rather delicate topological problems raised by such a choice.

The eigenfunctions provide irreps for the permutation group $\mathcal{S}$ of the system.

This group comprises the direct product of the permutation group $\mathcal{S}_N$ for the electrons with the permutation groups $\mathcal{S}_{A_i}$ for each set of identical nuclei i comprising A_i members.

The physically realisable irreps of this group are restricted by the requirement that, when spin is properly incorporated into the eigenfunctions, the eigenfunctions form a basis only for the totally symmetric representation, if bosons (spin 0, 1, 2 etc) or of the antisymmetric representation, if fermions (spin 1/2, 3/2, 5/2 etc). Both of these representations are one-dimensional.

In general the relevant spatial irreps will be many dimensional.

The extent of electronic degeneracy of a singlet state for a relatively simple hydrocarbon with empirical formula C_8H_8 and 56 electrons can be shown to be

$$53 \times 47 \times 44 \times 43 \times 41 \times 37 \times 35 \times 34 \times 31 \simeq 2.6\ 10^{14}$$

In view of the discussion by Born and Oppenheimer, express $\mathsf{H}'(\mathbf{t})$ in terms of two sets of coordinates

One set is expressed entirely in terms of the coordinates used originally to describe the nuclei, $\mathbf{x}_i^n$,

$$\mathbf{t}_i^n = \sum_{j=1}^{A} \mathbf{x}_j^n V_{ji}^n, \qquad i = 1, 2, \ldots, A-1$$

Here $\mathbf{V}^n$ is a non-singular matrix whose last column has elements

$$V_{iA}^n = M^{-1} m_i, \qquad\qquad M = \sum_{i=1}^{A} m_i$$

so that the coordinate $\mathbf{X}$ is the coordinate of the centre-of-nuclear mass.

The elements in the first $A-1$ columns of $\mathbf{V}^n$ each sum to zero, to ensure translational invariance.

The other set comprises N translationally invariant ‘electronic’ coordinates defined in terms of the initially chosen electronic variables $\mathbf{x}^e$ and whose origin is the centre-of-nuclear mass

$$\mathbf{t}_i^e = \mathbf{x}_i^e - \mathbf{X}$$

$$\mathsf{H}'(\mathbf{t}) \rightarrow \mathsf{H}^e(\mathbf{t}^e) + \mathsf{H}^n(\mathbf{t}^n) + \mathsf{H}^{en}(\mathbf{t}^n, \mathbf{t}^e)$$

$$\mathsf{H}^e(\mathbf{t}^e) = -\frac{\hbar^2}{2m}\sum_{i=1}^{N} \nabla^2(\mathbf{t}_i^e) - \frac{\hbar^2}{2M}\sum_{i,j=1}^{N} \vec{\nabla}(\mathbf{t}_i^e)\cdot\vec{\nabla}(\mathbf{t}_j^e) + \frac{e^2}{8\pi\epsilon_0}\sum_{i,j=1}^{N}{}' \frac{1}{|\mathbf{t}_j^e - \mathbf{t}_i^e|}$$

or

$$\mathsf{H}^e(\mathbf{t}^e) = -\frac{\hbar^2}{2\mu}\sum_{i=1}^{N} \nabla^2(\mathbf{t}_i^e) - \frac{\hbar^2}{2M}\sum_{i,j=1}^{N}{}' \vec{\nabla}(\mathbf{t}_i^e)\cdot\vec{\nabla}(\mathbf{t}_j^e) + \frac{e^2}{8\pi\epsilon_0}\sum_{i,j=1}^{N}{}' \frac{1}{|\mathbf{t}_j^e - \mathbf{t}_i^e|}$$

with

$$1/\mu = 1/m + 1/M$$

$$\mathsf{H}^n(\mathbf{t}^n) = -\frac{\hbar^2}{2}\sum_{i,j=1}^{A-1}\frac{1}{\mu_{ij}^n}\vec{\nabla}(\mathbf{t}_i^n).\vec{\nabla}(\mathbf{t}_j^n)$$

$+$

$$\frac{e^2}{8\pi\epsilon_0}\sum_{i,j=1}^{A}{}'\frac{Z_iZ_j}{r_{ij}(\mathbf{t}^n)}$$

$$r_{ij}(\mathbf{t}^n) = \left(\sum_{\alpha}(\sum_{k=1}^{A-1}((\mathbf{V}^{n-1})_{kj} - (\mathbf{V}^{n-1})_{ki})t_{\alpha k}^n)^2\right)^{1/2}$$

$$1/\mu_{ij}^n = \sum_{k=1}^{A} {m_k}^{-1}V_{ki}^nV_{kj}^n, \qquad i,j = 1,2,...A-1$$

$$\mathsf{H}^{en}(\mathbf{t}^n, \mathbf{t}^e) = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^{A} \sum_{j=1}^{N} \frac{Z_i}{r'_{ij}(\mathbf{t}^n, \mathbf{t}^e)}$$

$$|\mathbf{x}_i^n - \mathbf{x}_j^e| \equiv r'_{ij} = \left| \sum_{k=1}^{A-1} \mathbf{t}_k^n (\mathbf{V}^n)^{-1}_{ki} - \mathbf{t}_j^e \right|$$

By analogy with the BO approach in which nuclear motion is at first ignored the electronic Hamiltonian arising from our Hamiltonian on ignoring the nuclear motion is

$$\mathsf{H}^{\mathsf{elec}}(\mathbf{t}^{\mathsf{n}},\mathbf{t}^{\mathsf{e}}) = \mathsf{H}^{\mathsf{e}}(\mathbf{t}^{\mathsf{e}}) + \mathsf{V}^{\mathsf{en}}(\mathbf{t}^{\mathsf{n}},\mathbf{t}^{\mathsf{e}}) + \frac{e^2}{8\pi\epsilon_0}\sum_{i,j=1}^{A}{}' \frac{Z_i Z_j}{r_{ij}(\mathbf{t}^{\mathsf{n}})}$$

$$\mathsf{H}'(\mathbf{t}) = -\frac{\hbar^2}{2}\sum_{i,j=1}^{A-1}\frac{1}{\mu_{ij}^{n}}\vec{\nabla}(\mathbf{t}_i^n).\vec{\nabla}(\mathbf{t}_j^n) + \mathsf{H}^{\mathsf{elec}}(\mathbf{t}^{\mathsf{n}},\mathbf{t}^{\mathsf{e}})$$

If the $\mathbf{t}^{\mathsf{n}}$ were assigned values, $\mathbf{b}$ say, based upon choices $\mathbf{a}$ made in the laboratory-fixed frame, then

$$\mathsf{H}^{\mathsf{elec}}(\mathbf{t}^{\mathsf{n}}, \mathbf{t}^{\mathsf{e}}) \rightarrow \mathsf{H}^{\mathsf{elec}}(\mathbf{b}, \mathbf{t}^{\mathsf{e}})$$

This Hamiltonian is very like the usual clamped-nuclei one but it is explicitly translationally invariant and has an extra term, which is often called either the Hughes-Eckart or the mass polarisation term. The domain of $\mathsf{H}^{\mathsf{elec}}(\mathbf{b}, \mathbf{t}^{\mathsf{e}})$ consists of functions on $\mathbf{R}^{3N}$.

The Hamiltonian can be shown to have discrete solutions $\Psi_p^{\mathsf{elec}}(\mathbf{b}, \mathbf{t}^{\mathsf{e}})$ below the HVZ threshold

The Hamiltonian $\mathsf{H}^{\mathsf{elec}}(\mathbf{t}^{\mathsf{n}},\mathbf{t}^{\mathsf{e}})$ has a domain of functions on $\mathbf{R}^{3N}\otimes\mathbf{R}^{3(A-1)}$.

It contains a bare Coulomb operator involving the nuclear variables alone with no kinetic energy terms at all and the potential operator cannot, in this context, be regarded as small; there must therefore be some question about its self-adjointness.

The operator seems to be unbounded and to have a completely continuous spectrum of a very unpleasant kind given that eigenfunctions of the cartesian position operators are Dirac δ functions.

It is often assumed that the electronic problem can be written as if the potential for nuclear motion arose from:

$$\mathsf{H}^{\mathsf{elec}}(\mathbf{t}^{\mathsf{n}},\mathbf{t}^{\mathsf{e}})\Psi_p^{\mathsf{elec}}(\mathbf{t}^{\mathsf{n}},\mathbf{t}^{\mathsf{e}}) = E_p^{\mathsf{elec}}(\mathbf{t}^{\mathsf{n}})\Psi_p^{\mathsf{elec}}(\mathbf{t}^{\mathsf{n}},\mathbf{t}^{\mathsf{e}})$$

but from the forgoing discussion the problems in such an identification are apparent.

Note that the electronic Hamiltonian commutes with each of the $A-1$ nuclear position variables.

Think now of the molecular bound state space $\mathfrak{H}$ as the square integrable sections in the trivial fiber bundle $\mathbf{R}^{3A-6} \otimes \mathcal{L}^2(\mathbf{R}^{3N})$. In this case the the nuclear operator (which is the bare kinetic energy operator) acts in the base space, that is upon functions defined on $\mathbf{R}^{3A-6}$ and the electronic Hamiltonian acts only upon the fiber defined by the choice of $\mathbf{b}$.

Now write the full electronic Hamiltonian as a direct integral over the fibers.

$$\mathsf{H}^{\mathsf{elec}}(\infty, \mathbf{t}^{\mathsf{e}}) = \int_{\oplus} \mathsf{H}^{\mathsf{elec}}(\mathbf{b}, \mathbf{t}^{\mathsf{e}}) d\mathbf{b} \tag{1}$$

This is, of course to redefine the electronic Hamiltonian but in a perfectly reasonable way and one which avoids the pitfalls of trying to deal with it directly. It is a perfectly decent operator but it is, alas, not possible to use it directly to produce a potential surface $V^{elec}(\mathbf{t}^{\mathsf{n}})$. The most that can be done is to define a potential about a minimum. The position of that minimum is determined in the usual way as the point at which the lowest eigenvalue of the electronic Hamiltonian is a minimum. But the lowest eigenvalue expresed as a function of the relative nuclear coordinates cannot regarded as a potential in the usual way, except close to the minimum.

There are also some aspects of it that need a bit more discussion.

It should be noted that $\Psi^{\text{elec}}(\mathbf{b}, \mathbf{t}^{\text{e}})$ as a solution to the Schrödinger equation with $\mathbf{t}^{\text{n}}$ replaced by $\mathbf{b}$, is defined only up to a phase factor of the form

$$\exp[iw(\mathbf{b})]$$

where w is any single-valued real function of the $\mathbf{b}_k$ and can be different for different electronic states. Specific phase choices must therefore be made when tying this part to the nuclear part of the product wave function. It is only by making suitable phase choices that the electronic wave function is made a continuous function of the formal nuclear variables, $\mathbf{b}$, and the complete product function, made single valued. This is the origin of the Berry phase in clamped nuclei calculations involving intersecting potential energy surfaces.

If it is decided to treat the system by specifying a set of three rotation angles expressed in terms of the nuclear variables only and a set of internal coordinates invariant under orthogonal transformations then problems arise with the vector bundle idea. This is because such a separation requires that the the original vector space is decomposed into the manifold $\mathbf{S}^3 \otimes \mathbf{R}^{3A-6} \otimes \mathbf{R}^{3N}$. But this manifold cannot be coordinatised globally, of course, so any account of electronic structure given in this way can at best be only local.

If a solution of the electronic problem is to be used in a solution of the full problem then the solution must be one invariant under the permutation of identical nuclei. The direct integral form is indifferent to whether or not individual nuclei are identified and it is thus perfectly possible to regard formally identical nuclei as distinguishable particles simply by a suitable labeling of the points specified by $\mathbf{b}$. However it is equally possible that the direct integral properly reflect the permutational symmetry by requiring that if $\mathbf{b}'$ results from a permutation of identical nuclei specified by $\mathbf{b}$ both sets be included in the same way in the direct integral.

The fiber bundle approach to justify the BO approach for diatomics was used in 1979 by Combes and Seiler and for polyatomics in 1992 by Martinez and his coworkers. In the first case the rotational part of the problem could be separated off but in the second case it could not, because of the topological considerations mentioned earlier.

It is not possible in the fiber bundle approach to develop a general potential for nuclear motion. What an be shown is that if locally there is a lowest discrete eigenvalue of the electronic Hamiltonian, sufficiently well separated from the others, then within that locality it is possible to use a WKB expansion which in first approximation yields the complete eigenfunction as a product of electronic and a nuclear motion parts.

Although the electronic part is just the eigenfunction of the electronic Hamiltonian of lowest energy in the locality, the nuclear part is not an eigenfunction of the operator made up as the sum of the nuclear kinetic energy operators and the potential, because a potential in the usual sense cannot be precisely defined away from the minimum.

At present there has been no direct consideration of the Born and Huang approach by mathematicians.

However, in the time-dependent coherent states (wave-packet) approach to a freely moving system, it is possible to use the laboratory-fixed coordinate system and hence to deal with all the asymptotes, while avoiding problems arising from the pure translational continuum. This approach has been extensively developed by George Hagedorn beginning in 1980.

There is so far no mathematically satisfactory resolution of the general level crossing problem.

If the nuclei are treated as identifiable particles and a particular set of nuclear coordinates is chosen then any choice of nuclear coordinates that can be obtained from a given choice by means of a rotation-reflection will generate the same geometrical figure. Similarly any nuclear coordinate choice that arises from a permutation of nuclei with the same charge, will give rise to the same energy. However two equivalent geometries so generated usually correspond to a different coordinate choice. So, regarding the electronic energy as specifying a particular a point on a potential surface expressed in terms of the $\mathbf{t}_g^n$ is rather too restrictive. It actually corresponds to as many points as are generated by permutations of particles with identical charges together with all rotation-reflections.

In practical calculations the potential is taken to be invariant under rotation-reflections. This is to assume the as yet unsubstantiated assumption that rotational motion can be separated off in the BO approach. But permutational invariance is neither assumed nor generally enforced. It is usually simply ignored.

However at least as long ago as 1985 this invariance was considered by Schmelzer and Murrell and developed later in a series of papers by Collins and his group. If the chosen point is located at a minimum on the potential surface then it corresponds to a multiple minimum with as many wells as there are permuted positions.

The nuclear motion problem tackled along the lines of the Born Oppenheimer programme would thus involve establishing that the usual solutions were asymptotic solutions to a problem with a many-well potential. It would also involve constructing permutationally allowed trial functions for nuclear motion. No mathematical work that attempts to follow the Born and Oppenheimer or the Born programme along this path appears to have been done.

It would seem that it is not at present possible to give a a satisfactory account of how the usual clamped nuclei approach leads to a solution of the moving nuclei problem.

Of course if one identifies nuclei then one can certainly be confident about the BO approach and it makes perfect sense to work as we usually do. But even with the nuclei identified, the idea of a “global” potential surface seems to be a nonsense, and even if one can be satisfied with locally defined surfaces, unless the surface chosen is well separated from any other surface, its status is not too clear.