
Thierry Jecko¹, Brian T. Sutcliffe² and R. Guy Woolley³
²AGM, UMR 8088 du CNRS, Université de Cergy-Pontoise, Département de mathématiques, site de Saint Martin, 2 avenue Adolphe Chauvin, F-95000 Pontoise, France.
³Service de Chimie quantique et Photophysique, Université Libre de Bruxelles, B-1050 Bruxelles, Belgium
¹School of Science and Technology, Nottingham Trent University, Nottingham NG11 8NS, U.K.
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The paper [J. Chem.Phys. 138, 224110 (2013)] is the latest in a series of attempts to write the exact molecular wavefunction in electron-nuclear product form. We give reasons for supposing that this attempt fails to deliver what it promises.

Attempts to write the molecular wave function in an electron-nuclear product form are motivated by the need to develop an electronic Hamiltonian in terms of which molecular structure and potential energy surfaces (PES) can be described without appealing to the mathematically vague basis (see¹⁻³) provided by Born⁴ in the usual Born-Huang⁵ approach. The earliest attempt was made by Hunter⁶; later attempts were made by Gross⁷,⁸ using a time-dependent formulation and the most recent one, reverting to the time-independent formulation has been made by Cederbaum⁹.

Of these methods only that of Hunter has been tested on a system described by the Schrödinger Coulomb Hamiltonian; Czub and Wolniewicz¹⁰ showed that for the H₂ molecule Hamiltonian, Hunter’s idea did not yield the hoped for potential energy surface but rather one with spikes in it. Later work by Cassam-Chenai¹¹ using the standard electronic Hamiltonian showed that the spikes remained even though his method was close to the conventional one. It is our view that the latest approaches fail to construct an Hamiltonian that determines purely the electronic part of the problem, and that the best that can be done is to construct one that yields a decent approximation to a specified exact eigenstate.

Let us begin by recalling the formulation of the problem. A molecule considered as a quantum mechanical collection of electrons and nuclei is described by the usual Coulomb Hamiltonian \( \mathcal{H} \) with Schrödinger equation

\[
\mathcal{H} \Psi = E \Psi, \quad \mathcal{H} = \mathcal{H}_r + \mathcal{T}_N.
\]  

(1)

In the Born-Oppenheimer model the eigenvector \( \Psi \) is approximated as a simple product of normalized ‘electronic’ and ‘nuclear’ wavefunctions

\[
\Psi \approx \varphi(r, R) \chi(R), \quad \langle \varphi | \varphi \rangle_r = \langle \chi | \chi \rangle_R = 1
\]  

(2)

where \( \varphi \) is an eigenvector of the clamped nuclei Hamiltonian, and \( \chi \) is an eigenvector for the nuclear motion in the potential well associated with \( \varphi \). Can the \( \approx \) symbol in (2) be replaced by \( = \) with suitably redefined normalized ‘electronic’ and ‘nuclear’ functions \( \varphi \) and \( \chi \)?

First it must be said that either the centre-of-mass (CM) contribution must be removed from \( \mathcal{H} \) or the CM momentum must be fixed, otherwise \( \mathcal{H} \) has no eigenvalues since it describes a freely moving system. What is of interest is the internal motion relative to the centre-of-mass. This modification is easily made and we will interpret Cederbaum’s paper⁹ as though it had been done: note that in performing the separation of CM and internal motions, care must be taken to ensure that it remains possible to group the internal coordinates in such a way that electrons and nuclei remain identifiable.

The proposed factorization of \( \Psi \) is first discussed in §IIA in a direct fashion in which the product ansatz is substituted into (1) and equations for \( \varphi \) and \( \chi \) are derived⁹. The key point here seems to be an identification of an ‘electronic’ contribution to the energy

\[
\mathcal{H}_e \varphi = \mathcal{E}_e(R) \varphi
\]  

(3)

with

\[
\mathcal{H}_e = \mathcal{H} - \hbar^2 / 2M (\nabla \ln \chi \cdot \nabla)
\]  

(4)

and both factors, \( \varphi \chi \) supposed ‘normalized’ to unity in the sense that

\[
\langle \varphi | \varphi \rangle_r = \langle \chi | \chi \rangle_R = 1.
\]  

(5)

With this condition, and for real valued \( \varphi \), the ‘electronic’ energy \( \mathcal{E}_e(R) \) is

\[
\mathcal{E}_e(R) = \langle \varphi | \mathcal{H} | \varphi \rangle_r.
\]  

(6)

In case \( \varphi \) is complex, \( \mathcal{H} \) in (6) must be replaced by \( \mathcal{H}_e \).

In §IIIB the author proposes a variational approach to the solution of (1) that utilizes trial functions in the product form \( \varphi \chi \). A precise formulation of the idea is as follows: let \( \mathcal{H} \) be the space of admissible states \{\( \Psi \)\}, and \( \mathcal{E} \) the set of eigenvalues of \( \mathcal{H} \). Let \( \mathcal{H}_0 \) be the subset of \( \mathcal{H} \) formed by vectors in the product form¹² \( \varphi \chi \) for admissible \( \varphi \) and \( \chi \). The admissible states are square-integrable in all their variables, hence normalizable¹². Consider the functional¹³ \( \tau : \mathcal{H}_0 \times \mathbb{R}^2 \to \mathbb{R} \) specified by

\[
((\varphi, \chi); (\lambda, \mu)) \mapsto \langle \varphi | \mathcal{H} | \varphi \rangle + \lambda \left( 1 - ||\varphi \chi||^2 \right) + \mu \left( 1 - ||\chi||_R^2 \right).
\]  

(7)

Cederbaum claims that direct calculation shows that a critical (or stationary) point of the functional \( \tau \), say \((\varphi_\lambda, \chi_\lambda); (\lambda_\mu, \mu)\) satisfies

\[
\mu_\lambda = 0, \quad ||\chi_\lambda||_R = 1, \quad ||\varphi(r, \lambda)||_r = 1
\]  

(8)

\[
(\varphi_\lambda, \chi_\lambda) \in \mathcal{H}_0
\]  

(9)

\[
\mu_\mu = 1
\]  

(10)

\[
(\varphi_\mu, \chi_\mu) \in \mathcal{H}_0
\]  

(11)
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τ

variational approach in

valid representation of Ψ. On the other hand, while the

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the traditional sense of being the solution of a differential

an 'electronic' operator ?

appears in the equation for the other, and that their

linear equation such as (3) does not contain a disposable

χ

interactions does not have

the Born-Oppenheimer approximation; more specifically

in the latter equation there should

exclude this possibility, nor is there any longer a reason

require b = 1 for all R.

One may reasonably ask whether this is really at all

in the spirit of the electron-nuclear separation offered by

Cederbaum’s equation (16c) to (16d); in the latter equation there should not be a factor of b

as a denominator of the last term in the equation. The

calculation then continues but yields only the first two conditions in (8) above with (6) modified to read,

provided b(R) ≠ 0; there is nothing in the calculation to exclude this possibility, nor is there any longer a reason

to require b = 1 for all R.

It must also be noted that each of the functions ϕ, χ appears in the equation for the other, and that their

defining equations are non-linear. The solution of a non-

linear equation such as (3) does not contain a disposable

multiplicative constant so that a solution of (3) satisfying

(5) simply may not exist. Most pertinently the factor-

ization is simply assumed in §IIA, and nothing is offered in

this section that leads towards a proof that it is a

valid representation of Ψ. On the other hand, while the

variational approach in §IIIB may yield a factorized eigenvector if τ has a critical point, the existence of a critical point is not demonstrated.

Concerning the proposed completely solvable model based on coupled oscillators involving light and heavy

masses, it is highly pertinent to note that coupled har-

monic oscillator systems are integrable because of an un-

derlying abstract symmetry of the problem, so that an

exact solution can always be produced in a product form

by separation of variables. A system of light and heavy

particles involving Coulomb interactions does not have

this symmetry, and in general is not integrable. In our

view a comparison between the quantum mechanics of

two such systems with such different formal properties is

simply not instructive; the occurrence of light and heavy

particles in the two systems is not really relevant to a dis-

cussion of the structure of their associated eigenvectors.

One might hope to simplify Cederbaum’s scheme by

choosing at the outset one of the factors; for example we

know that the exact eigenvectors Ψ, satisfy a bound de-

scribing exponential decay so one could reasonably

choose (R) as some exp (−f(R)) belonging to

that is real and vanishes nowhere. The formalism of §IIA can

then be followed through, with now explicit, and the

problem reduces to the determination of ϕ(r, R); how-

ever it is quite evident that this results simply in the

complexity of the original problem (1) being transferred

to the determination of ϕ. It seems to us pertinent to

observe that every eigenvector of (1) belongs to an irre-

ducible representation of each of the invariance groups of

the molecular Hamiltonian (angular momentum, time

and space reversal, permutation symmetry) and it is dif-

ficult to avoid the conclusion that any proposed factor-

ization of each eigenvector Ψ, will involve quite distinct ‘electronic’ and ‘nuclear’ functions. Thus there would

be no clear evidence of the hierarchy of energy levels

(‘electronic’, ‘vibrational’, ‘rotational’) associated with

factorized wavefunctions of the form \( \phi \chi \), that was the great success of the original work of Born and

Oppenheimer.


12In view of the occurrence of \( T \chi \) in H, the admissible states must actually belong to the Sobolev space, \( H^2 \), since we require func-

13tions with derivatives up to second order that are also normaliz-

able; \( H^2 \) is a subspace of \( L^2 \).

