Comment on 'The exact molecular wavefunction as a product of an electronic and nuclear wavefunction' [J. Chem.Phys. 138, 224110 (2013)]

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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 (see[1–3]) provided by Born[4] in the usual Born-Huang[5] approach. The earliest attempt was made by Hunter[6]; later attempts were made by Gross[7,8] using a time-dependent formulation and the most recent one, reverting to the time-independent form has been made by Cederbaum[9].

Of these methods only that of Hunter has been tested on a system described by the Schrödinger Coulomb Hamiltonian; Czub and Wolniewicz[10] showed that for the H_2 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-Chenai[11] 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 H with Schrödinger equation

$$\mathsf{H}\Psi = E\Psi, \quad \mathsf{H} = \mathsf{H}_{el} + \mathsf{T}_N. \tag{1}$$

In the Born-Oppenheimer model the eigenvector Ψ is approximated as a simple product of normalized 'electronic' and 'nuclear' wavefunctions

$$\Psi \approx \varphi(r,R)\chi(R), \quad \langle\varphi|\varphi\rangle_r = \langle\chi|\chi\rangle_R = 1 \tag{2}$$

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

First it must be said that either the centre-of-mass (CM) contribution must be removed from H or the CM momentum must be fixed, otherwise 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 paper[9] 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 Ψ is first discussed in §IIA in a direct fashion in which the product ansatz is substituted into (1) and equations for $\overline{\varphi}$ and $\overline{\chi}$ are derived[9]. The key point here seems to be an identification of an 'electronic' contribution to the energy

$$\overline{\mathsf{H}}_{el}\overline{\varphi} = \overline{E}_{el}(R)\overline{\varphi} \tag{3}$$

with

$$\overline{\mathsf{H}}_{el} = \mathsf{H} - \frac{\hbar^2}{2M}\big(\nabla \ln \overline{\chi} \cdot \nabla\big) \tag{4}$$

and both factors, $\overline{\varphi}, \overline{\chi}$ supposed 'normalized' to unity in the sense that

$$\langle\overline{\varphi}|\overline{\varphi}\rangle_r = \langle\overline{\chi}|\overline{\chi}\rangle_R = 1. \tag{5}$$

With this condition, and for real valued $\overline{\varphi}$, the 'electronic' energy $\overline{E}_{el}(R)$ is

$$\overline{E}_{el}(R) = \langle\overline{\varphi}|\mathsf{H}|\overline{\varphi}\rangle_r. \tag{6}$$

In case $\overline{\varphi}$ is complex, H in (6) must be replaced by $\overline{\mathsf{H}}_{el}$.

In §IIB the author proposes a variational approach to the solution of (1) that utilizes trial functions in the product form $\overline{\varphi}\ \overline{\chi}$. 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 H. Let $\mathcal{H}_0$ be the subset of $\mathcal{H}$ formed by vectors in the product form[12] $\overline{\varphi}\ \overline{\chi}$ for admissible $\overline{\varphi}$ and $\overline{\chi}$. The admissible states are square-integrable in all their variables, hence normalizable[12]. Consider the functional[9] $\tau : \mathcal{H}_0 \times \Re^2 \to \Re$ specified by

$$\begin{aligned}\big((\overline{\varphi},\overline{\chi});(\lambda,\mu)\big) \mapsto \langle\overline{\varphi}\ \overline{\chi}|\mathsf{H}|\overline{\varphi}\ \overline{\chi}\rangle + \lambda\left(1 - ||\overline{\varphi}\ \overline{\chi}||^2\right) \\ + \mu\left(1 - ||\overline{\chi}||_R^2\right).\end{aligned} \tag{7}$$

Cederbaum claims that direct calculation shows that a *critical* (or stationary) point of the functional τ, say $\big((\overline{\varphi}_i,\overline{\chi}_i);(\lambda_i,\mu_i)\big)$ satisfies

$$\mu_i = 0, \quad ||\overline{\chi}_i||_R = 1, \quad ||\overline{\varphi}(r,R)_i||_r = 1 \tag{8}$$

and $\overline{\varphi}_i, \overline{\chi}_i$ solve his equations (18a),(18b); this would imply that the product $\overline{\varphi}_i\overline{\chi}_i$ is an eigenvector of H and λ_i belongs to $\mathcal{E}$.

Unfortunately there is a mistake in the calculation presented; for ease of notation, define

$$\langle\overline{\varphi}|\overline{\varphi}\rangle_r = b \tag{9}$$

and note that *a priori*, $b = b(R)$. The mistake is in the passage from 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,

$$\overline{E}_{el}(R) = \frac{\langle\overline{\varphi}|\mathsf{H}_{el}|\overline{\varphi}\rangle_r}{b(R)} \tag{10}$$

provided $b(R) \neq 0$; there is nothing in the calculation to exclude this possibility, nor is there any longer a reason to require $b = 1$ for all R.

One may reasonably ask whether this is really at all in the spirit of the electron-nuclear separation offered by the Born-Oppenheimer approximation; more specifically how can the operator $\overline{\mathsf{H}}_{el}$ that involves nuclear position (through $\overline{\chi}$) and momentum variables be described as an 'electronic' operator ? $\overline{\varphi}$ is not an electronic state in the traditional sense of being the solution of a differential equation in the electronic (r) variables with R-dependent coefficients. In any case $\overline{\mathsf{H}}_{el}$ is ill-defined when $\overline{\chi}$ vanishes somewhere.

It must also be noted that each of the functions $\overline{\varphi}$, $\overline{\chi}$ 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 factorization 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 §IIB 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 harmonic oscillator systems are *integrable* because of an underlying 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 discussion 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_i satisfy a bound describing exponential decay[13,14] so one could reasonably choose $\overline{\chi}(R)$ as some $\exp(-f(R))$ belonging to $\mathcal{H}^2$ that is real and vanishes nowhere. The formalism of §IIA can then be followed through, with now $\overline{\chi}$ explicit, and the problem reduces to the determination of $\overline{\varphi}(r, R)$; however it is quite evident that this results simply in the complexity of the original problem (1) being transferred to the determination of $\overline{\varphi}$. It seems to us pertinent to observe that every eigenvector of (1) belongs to an irreducible representation of each of the invariance groups of the molecular Hamiltonian H (angular momentum, time and space reversal, permutation symmetry) and it is difficult to avoid the conclusion that any proposed factorization of each eigenvector Ψ_i 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 $\phi_{\mathrm{el}}\chi_{\mathrm{vib}}\eta_{\mathrm{rot}}$ that was the great success of the original work of Born and Oppenheimer[15].

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[12] In view of the occurrence of T_N in H, the admissible states must actually belong to the Sobolev space, $\mathcal{H}^2$, since we require functions with derivatives up to second order that are also normalizable; $\mathcal{H}^2$ is a subspace of L^2.

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