Norm conservation in A. Abedi, N. T. Maitra and E. K. U. Gross, J. Chem. Phys. 137, 22A530, 2012

J. L. Alonso,^{1,2,3} J. Clemente-Gallardo,^{1,2,3} P. Echenique,^{4,1,2,5,3} and J. A. Jover-Galtier^{1,2}

¹Departamento de Física Teórica, Universidad de Zaragoza, Pedro Cerbuna 12, E-50009 Zaragoza, Spain

²Instituto de Biocomputación y Física de Sistemas Complejos (BIFI),

Universidad de Zaragoza, Mariano Esquillor s/n, Edificio I+D, E-50018 Zaragoza, Spain

³Unidad Asociada IQFR-BIFI, Mariano Esquillor s/n, Edificio I+D, E-50018 Zaragoza, Spain

⁴Instituto de Química Física Rocasolano, CSIC, Serrano 119, E-28006 Madrid, Spain

⁵Zaragoza Scientific Center for Advanced Modeling (ZCAM), Universidad de Zaragoza, Mariano Esquillor s/n, Edificio I+D, E-50018 Zaragoza, Spain

(Dated: February 26, 2013)

In spite of the relevance of the proposal introduced in the recent work A. Abedi, N. T. Maitra and E. K. U. Gross, *J. Chem. Phys.* **137**, 22A530, 2012, there is an important ingredient which is missing. Namely, the proof that the norms of the electronic and nuclear wavefunctions which are the solutions to the nonlinear equations of motion are preserved by the evolution. To prove the conservation of these norms is precisely the objective of this Comment.

In a remarkable recent work [1], Abedi et al. present an exact factorization of the molecular wavefunction into a nuclear and an electronic part, which allows to rigorously introduce generalized and very useful concepts, such as the time-dependent potential energy surface. This formalism also sets the stage to better understand, and hence probably improve, very much used quantumclassical schemes, such as Ehrenfest, surface-hopping or Born-Oppenheimer dynamics.

In spite of the relevance of the proposal, we consider that there is an important ingredient which is missing. Namely, the proof that the norms of the two functions $\Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},t)$ and $\chi(\underline{\mathbf{R}},t)$, which are solutions of the nonlinear Eqs. (28) and (29) in [1]. This is a key point in order to associate $\Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},t)$ and $\chi(\underline{\mathbf{R}},t)$ to a marginal and a conditional probability amplitude, respectively, thus leading to their identification as nuclear and electronic wavefunctions, as it is the purpose of [1].

If one wants to be sure that a given set of equations of motion do conserve any given quantity, there are essentially two options: Either one explicitly forces the conservation at the action level, e.g., using Lagrange multipliers, or one shows that there is another reason (e.g., a symmetry of the action) why the obtained equations of motion produce the conservation. In [1], neither of these two things are explicitly done.

In these works it is proved that the exact solution, $\Psi(\underline{\mathbf{R}}, \underline{\mathbf{r}}, t)$, of the time-dependent molecular Schrödinger equation can be written as a single product of the form

$$\Psi(\underline{\mathbf{R}}, \underline{\mathbf{r}}, t) = \Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}}, t)\chi(\underline{\mathbf{R}}, t) , \qquad (1)$$

such that the partial normalization condition (PNC),

$$\int d\underline{\mathbf{r}} |\Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},t)|^2 = 1 \qquad \forall \underline{\mathbf{R}},t , \qquad (2)$$

is satisfied. This condition implies that also χ is normalized if Ψ is.

But the PNC is only used in [1] to simplify the Euler-Lagrange equations once they have been obtained from the stationary action principle. As we said, since the conservation has not been enforced at the action level from the very first step, this occasional use of the PNC does not guarantee, in principle, that it holds for all times if no further proof is provided.

But, before detailing our proof of this property does hold, let point out that two possible ways of proving it have been discarded here for different reasons. First, one could have shown that the action has a certain symmetry and obtain the conservation law as an application of Noether's theorem. We have been unable to find such a symmetry. Second, notice that the equations of motion in [1] can be written as

$$i\partial_t \Phi_{\mathbf{R}}(\mathbf{\underline{r}},t) = \hat{H}_{\Phi}[\Phi_{\mathbf{R}},\chi,\partial_t \Phi_{\mathbf{R}}] \Phi_{\mathbf{R}}(\mathbf{\underline{r}},t) ,$$
 (3a)

$$\hat{\partial}_t \chi(\underline{\mathbf{R}}, t) = \hat{H}_{\chi}[\Phi_{\underline{\mathbf{R}}}, \chi, \partial_t \Phi_{\underline{\mathbf{R}}}] \chi(\underline{\underline{\mathbf{R}}}, t) .$$
 (3b)

If the operators \hat{H}_{Φ} and \hat{H}_{χ} were linear and Hermitian, the conservation of the norm of the functions χ and $\Phi_{\underline{\mathbf{R}}}$ would be straightforward. As that is not the case, a more careful analysis is in order. In the literature, sometimes this type of problems are solved in a formal way. For some nonlinear cases, this formal procedure is useful and, assuming that all necessary conditions on the corresponding infinite dimensional Hilbert spaces are satisfied, it allows us to prove the conservation of the norm of the functions in a very simple way. However, in this particular case, and due to the dependence of the time derivative of $\Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},t)$ in the definition of the operators, the only way to have Hermiticity is to show in advance that the norm of $\Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},t)$ is indeed conserved. This renders the reasoning circular, and thus invalid.

The problem of obtaining the dynamical equations can be addressed from a different perspective. Consider then a decomposition of the form given by Eq. (1) but without imposing the PNC condition. In this case, we define:

$$f(\underline{\mathbf{\underline{R}}},t) := \int d\underline{\underline{\mathbf{r}}} |\Phi_{\underline{\mathbf{\underline{R}}}}(\underline{\mathbf{\underline{r}}},t)|^2 , \qquad (4)$$

and, if we use that Ψ is normalized at all times, we have:

$$\int d\underline{\underline{\mathbf{R}}} f(\underline{\underline{\mathbf{R}}}, t) |\chi(\underline{\underline{\mathbf{R}}}, t)|^2 = 1 .$$
(5)

If we consider this factorization for Ψ and introduce it in the variational framework used in [1], we obtain as dynamical equations:

$$if\partial_t \chi = \left[f(\hat{T}_n + \hat{V}_n) - i \sum_{\alpha=1}^{N_n} \frac{1}{M_\alpha} (\vec{\mathbf{A}}_\alpha \cdot \vec{\nabla}_\alpha) + \langle \Phi_{\underline{\mathbf{R}}} | \hat{T}_e + \hat{T}_n + \hat{V}_e + \hat{W}_{en} - i\partial_t | \Phi_{\underline{\mathbf{R}}} \rangle \right] \chi , \qquad (6)$$

$$if\partial_t \Phi_{\underline{\underline{\mathbf{R}}}} |\chi|^2 = \left[|\chi|^2 \left(f[\hat{T}_e + \hat{T}_n + \hat{V}_e + \hat{W}_{en}] - \langle \Phi_{\underline{\underline{\mathbf{R}}}} | (\hat{T}_e + \hat{T}_n + \hat{V}_e + \hat{W}_{en} - i\partial_t) | \Phi_{\underline{\underline{\mathbf{R}}}} \rangle \right) - \chi^* \sum_{\alpha=1}^{N_n} \frac{1}{M_\alpha} \left(f(\vec{\nabla}_\alpha \chi) \vec{\nabla}_\alpha + i\vec{A}_\alpha \cdot (\vec{\nabla}_\alpha \chi) \right) \right] \Phi_{\underline{\underline{\mathbf{R}}}} , \quad (7)$$

where the dependencies have been omitted, and

$$\hat{V}_{e}(\underline{\mathbf{r}},t) := \hat{W}_{ee}(\underline{\mathbf{r}}) + \hat{V}_{ext}^{e}(\underline{\mathbf{r}},t) ,$$

$$\hat{V}_{n}(\underline{\mathbf{R}},t) := \hat{W}_{nn}(\underline{\mathbf{R}}) + \hat{V}_{ext}^{n}(\underline{\mathbf{R}},t)$$

using the notation in [1].

These equations are completely general. Any factorization of the form (1), where the molecular wave function Ψ is a solution of the molecular Schrödinger equation, satisfies them. Also, notice that, if we have $f(\mathbf{\underline{R}}, t) = 1$ for all t (i.e., the factorization satisfies the PNC for all values of time), then these equations reduce to Eqs. (28) and (29) in [1]. Now, the factorization in (1) exhibits an invariance under the group of invertible functions on $\mathbb{C}_0 = \mathbb{C} - \{0\}$ given by

$$\begin{cases} \tilde{\chi}(\underline{\mathbf{R}},t) = a(\underline{\mathbf{R}},t)\chi(\underline{\mathbf{R}},t) ,\\ \tilde{\Phi}_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},t) = \frac{1}{a(\underline{\mathbf{R}},t)}\Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},t) , \end{cases}$$
(8)

where $a(\underline{\mathbf{R}}, t)$ is any complex function without zeros. In other words, for any given solution, $\chi(\underline{\mathbf{R}}, t)$ and $\Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}}, t)$, of the equations of motion in (6) and (7), we can obtain new solutions, $\tilde{\chi}(\underline{\mathbf{R}}, t)$ and $\tilde{\Phi}_{\underline{\mathbf{R}}}(\underline{\mathbf{r}}, t)$, which produce the same molecular wavefunction $\overline{\Psi}(\underline{\mathbf{R}}, \underline{\mathbf{r}}, t)$, by applying the above transformation. Of course, these new functions will be solution to the equations with the corresponding $\tilde{f}(\underline{\mathbf{R}}, t)$. Also notice that this gauge freedom enlarges the $U(\overline{1})$ -freedom discussed in [1], where only the phase of each function is transformed. Let us consider now a gauge fixing defined as

$$a(\underline{\underline{\mathbf{R}}},t) = e^{i\theta(\underline{\underline{\mathbf{R}}},t)}\sqrt{f(\underline{\underline{\mathbf{R}}},t)}$$
(9)

where $f(\underline{\mathbf{R}}, t)$ is defined by Equation (4) and $\theta(\underline{\mathbf{R}}, t)$ is arbitrary. Notice that we are extending the usual notion of gauge fixing in a subtle way. The transformation is considered for the full trajectory $\Psi(\underline{\mathbf{R}}, \underline{\mathbf{r}}, t)$, since it depends explicitly on the norm of the function $\Phi_{\underline{\mathbf{R}}}$ along it. Thus it becomes a dynamical property. In particular, if we consider a solution with initial unit norm, i.e., $f(\underline{\mathbf{R}}, 0) = 1, \forall \underline{\mathbf{R}}$, we find that the initial conditions for the original and the transformed curves coincide:

$$\tilde{\chi}(\underline{\mathbf{R}},0) = \chi(\underline{\mathbf{R}},0) , \qquad \tilde{\Phi}_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},0) = \Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},0) , \quad (10)$$

and that functions $\tilde{\Phi}_{\underline{\mathbf{R}}}$ and $\tilde{\chi}$ are normalized by construction for all values of time:

$$\int d\underline{\mathbf{R}} |\tilde{\chi}(\underline{\mathbf{R}},t)|^2 = 1 = \int d\underline{\mathbf{r}} |\tilde{\Phi}_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},t)|^2 \qquad \forall t, \underline{\mathbf{R}} \ . \ (11)$$

Finally, consider any solution of Eqs. (28) and (29)in [1] for some initial conditions $\chi^0(\underline{\mathbf{R}})$ and $\Phi^0_{\mathbf{R}}(\underline{\mathbf{r}})$ that satisfy the PNC, and let us ask whether or not the PNC is satisfied at subsequent times. We have seen that, among the factorizations of the molecular wavefunction $\Psi(\mathbf{\underline{R}},\mathbf{\underline{r}},t)$ [with initial conditions $\Psi(\mathbf{\underline{R}},\mathbf{\underline{r}},0) =$ $\chi^0(\underline{\mathbf{R}})\Phi^0_{\mathbf{R}}(\underline{\mathbf{r}}))$ there is one, given by $\tilde{\chi}(\underline{\mathbf{R}},t)$ and $\Phi_{\underline{\mathbf{R}}}(\underline{\mathbf{r}},t)$, which satisfies the PNC for all values of time, and also Eqs. (6–7) with $f(\mathbf{\underline{R}}, t) = 1$ and initial conditions $\chi^0(\mathbf{\underline{R}})$ and $\Phi^{0}_{\underline{\mathbf{R}}}(\underline{\underline{\mathbf{r}}})$. Now, given that Eqs. (6–7) with $f(\underline{\underline{\mathbf{R}}},t) = 1$ are precisely Eqs. (28) and (29) in [1], we have that the functions $\tilde{\chi}(\mathbf{\underline{R}},t)$ and $\tilde{\Phi}_{\mathbf{\underline{R}}}(\mathbf{\underline{r}},t)$ are a also a solution to them, with initial conditions $\chi^0(\underline{\mathbf{R}})$ and $\Phi^0_{\mathbf{R}}(\underline{\mathbf{r}})$, and such that their norms are preserved for all time. Since we have not modified the initial conditions, if we assume that Eqs. (28) and (29) in [1] have unique solution for given initial conditions, we can conclude that the normconserving solution to them that we have found must be the arbitrary one we began with, thus showing that every solution of Eqs. (28) and (29) in [1] with initial conditions that satisfy the PNC also satisfies it at all times.

ACKNOWLEDGEMENTS

We would like to thank Dr. Alberto Castro for many useful discussions. This work has been supported by grants FIS2009-13364-C02-01 (MICINN, Spain), and Grants E24/1 and E24/3 (DGA, Spain).

 A. Abedi, N. T. Maitra, and E. K. U. Gross, J. Chem. Phys. 137, 22A530 (2012).