Comment on "Optimization of approximate solutions to the time-dependent Schrödinger equation"

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In a previous work [A. B. Weglein, Phys. Rev. A **17**, 1810 (1978)], an optimization method to approximate solutions to the time-dependent Schrödinger equation proposed by Chang and Rapp was further developed. We show that, if correct in a mathematical sense, it leads to results which are physically inadequate.

The time-dependent Schrödinger equation

$$\left(H - i\frac{d}{dt}\right)|\psi\rangle = 0 \tag{1}$$

is usually solved approximating the solution by a trial wave function $|\psi_{\rm tr}\rangle$, which contains a set of optimizable parameters. The standard method[1] consists of taking a given subspace and making a linear parametrization. The coefficients are chosen so that the subspace-projected Schrödinger Eq. (1) is satisfied. A new optimization method has been proposed by Chang and Rapp.[2] It assumes that the trial wave function minimizes the deviation

$$J = \int_{t_i}^{t_f} \langle \epsilon | \epsilon \rangle \, dt \ , \tag{2}$$

where

$$|\epsilon\rangle = \left(H - i\frac{d}{dt}\right)|\psi_{\rm tr}\rangle \ . \tag{3}$$

In a subsequent work,[3] which we shall discuss here, a set of differential equations for the linear coefficients was developed, in order to minimize J. It must be noted that the norm of the trial wave function is not conserved in this development. This fact is, in the author's words, a "further support" for the interpretation that "in some way the values of P_{α_j} partly compensate for the effect of the missing states which were not included in $|\psi_{\rm tr}\rangle$." The perturbation potentials considered in Ref. 3 are those ones satisfying $V(t) \to 0$ as $t \to \mp\infty$. So, the transitions must vanish in these asymptotic regions. The author claims that this physical condition can be satisfied by selecting a given phase factor at the initial time. The aim of the present work is to prove the following. (1) The norm variation is not due to a probability flux to the missing states but to the natural tendency (in a mathematical sense) to the zero function. This is the case *for all perturbations which cannot be treated exactly.* (2) In the particular case of perturbations where $V(t) \to 0$ asymptotically, unphysical transitions in the initial unperturbed region cannot be eliminated. (3) It is possible to force the norm conservation in the J minimization but it leads to nonlinear equations with crossed boundary conditions.

Let us write, in a more general and compact form, the equations developed in Sec. IV of Ref. 3:

$$\dot{\alpha}_j = P_{\alpha_j^*} - i\langle \phi_j | \tilde{\epsilon} \rangle \ , \tag{4a}$$

$$\dot{P}_{\alpha_j^*} = -i\langle e_j | \tilde{P} \rangle + \langle e_j | (1-Q) | \tilde{\epsilon} \rangle \ , \tag{4b}$$

where $j = 1, 2, \ldots, n$ and

$$|\psi_{\rm tr}\rangle = \sum_{j=1}^{n} \alpha_j |\phi_j\rangle \ , \tag{5a}$$

$$P_{\alpha_j^*} = \frac{\partial}{\partial \dot{\alpha}_j^*} \langle \epsilon | \epsilon \rangle \ , \tag{5b}$$

$$|\tilde{\epsilon}\rangle = V|\psi_{\rm tr}\rangle \ , \tag{5c}$$

$$|e_j\rangle = V|\phi_j\rangle \ , \tag{5d}$$

$$|\tilde{P}\rangle = \sum_{j=1}^{n} P_{\alpha_j^*} |\phi_j\rangle \ , \tag{5e}$$

$$Q = \sum_{j=1}^{n} |\phi_j\rangle \langle \phi_j| \ . \tag{5f}$$

The J minimization has the only restriction $|\delta\psi_{\rm tr}(t_i)\rangle = 0$. Thus, the boundary conditions for Eqs. (4) are

$$\alpha_j(t_i) = \delta_{1j}, \quad P_{\alpha_j^*}(t_f) = 0 \ . \tag{6}$$

The solution of Eqs. (4) leads to an error

$$\langle \epsilon | \epsilon \rangle = \langle \tilde{P} | \tilde{P} \rangle + \langle \tilde{\epsilon} | (1-Q) | \tilde{\epsilon} \rangle$$
$$= \sum_{j=1}^{n} |P_{\alpha_j^*}|^2 + \langle \psi_{\rm tr} | V^2 - VQV | \psi_{\rm tr} \rangle \ . \tag{7}$$

Making use of (4), we obtain in (7)

$$\langle \epsilon | \epsilon \rangle = \sum_{j=1}^{n} (\dot{\alpha}_j^* P_{\alpha_j^*} + \alpha_j^* \dot{P}_{\alpha_j^*}) \ . \tag{8}$$

Integrating this expression and using (6), we obtain

$$J = -P_{\alpha_1^*}(t_i)\alpha_1(t_i) = -P_{\alpha_1^*}(t_i) \ . \tag{9}$$

Also, from (8) and (4), the time variation of the norm $N = \langle \psi_{\rm tr} | \psi_{\rm tr} \rangle$, results

$$\dot{N}(t) = \sum_{j=1}^{n} (\alpha_j P_{\alpha_j^*}^* + \alpha_j^* P_{\alpha_j^*}) = -2\int_{t}^{t_f} \langle \epsilon | \epsilon \rangle \, dt' \leq 0 \ . \tag{10}$$

Equation (10) shows that $\dot{N}(t)=0$ if and only if $|\epsilon\rangle=0$ for all $t'>t$. So, *the norm decreases at any time,* except when the trial wave function is capable of solving exactly Eq. (1) at each future time. However, this last case is irrelevant in the present discussion, where an approximation method is analyzed. This tendency to the zero function is due to the presence of the momenta $P_{\alpha_j^*}$ [see Eq. (10)]. These momenta contribute to the error but this contribution is widely compensated by the norm reduction in the last sum term of (7).

The unphysical consequence of this norm reduction becomes apparent when the integration interval t_f-t_i is sufficiently large: the zero function is obtained at the final time.

Equation (10) shows that $\dot{N}(t_i)=-2J$. This result is independent of the value of the perturbation at t_i. The corresponding transitions in the unperturbed initial region (which are related to the nonzero momenta at t_i) cannot be eliminated selecting a given phase factor at the initial time. This phase is irrelevant since the system of coupled equations (4) is invariant under multiplication by an arbitrary constant and this transformation does not modify the zero final condition for the momenta $P_{\alpha_j^*}$. Besides, Eq. (9) shows that the phases of $\alpha_1(t_i)$ and $P_{\alpha_1^*}(t_i)$ are not independent because J is real.

It must be noted that the standard close-coupling equations and the corresponding deviation can be obtained letting $P_{\alpha_j^*}\equiv 0$ in (4a) and (7), respectively. This deviation, as well as the time variation of the linear parameters, are due exclusively to the presence of the perturbation. So, there is no contribution from regions where this perturbation vanishes. This is not the case for the present analyzed method, which leads to nonzero constants $P_{\alpha_j^*}$ in those regions [see Eq. (9) and the above result $\dot{N}<0$].

In principle, it is possible to force the norm conservation for all time. Applying the Legendre multiplicator technique, we have obtained a set of coupled equations which differ with respect to Eqs. (4) in the presence of a new nonlinear term $-\langle\epsilon|\epsilon\rangle\alpha_j$, in the right-hand side of (4b). When solved for one state ($n=1$), the standard close-coupling result is obtained:

$$\alpha(t)=\exp\left(-i\int_{t_i}^{t}\langle\psi_{\rm tr}|V|\psi_{\rm tr}\rangle\,dt'\right)$$

and $P_{\alpha^*}(t)\equiv 0$.

However, in the general case ($n>1$), the new nonlinear equations are not equivalents to the standard ones and cannot be solved using the standard numerical method for linear systems with crossed boundary conditions (linear combinations of arbitrary $2n$ solutions). Besides, unphysical transitions between states $|\phi_j\rangle$ ($j=1,2,\ldots,n$) are not eliminated.

In conclusion, the present analyzed optimization method, if correct in a mathematical sense, leads to results which are physically inadequate. Consequently, it cannot be argued that it is a good alternative to the close-coupling method extensively employed, for example, in the treatment of atomic collisions. Even when the norm conservation is imposed, it is of doubtful practical utility.

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[1]M. R. McDowell and J. P. Coleman, *Introduction to the Theory of Ion-Atom Collisions* (North-Holland, Amsterdam, 1970).

[2]C. Chang and D. Rapp, J. Chem. Phys. **59**, 972 (1973).

[3]A. B. Weglein, Phys. Rev. A **17**, 1810 (1978).