Convergence of transition amplitudes obtained with the Schwinger variational principle

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An exactly solvable time-dependent quantum mechanical problem is employed to study the convergence properties of transition amplitudes calculated by using the Schwinger variational principle. A detailed comparison between the amplitudes approximated by the perturbative series and by their associated Schwinger variational principles is performed. The much better performance obtained by the variational principle is documented through different case studies. For a given order of the Schwinger principle, it is observed that the transition amplitudes do not converge to the exact one for large perturbations. The latter is true even though large combinations of unperturbed states with constant coefficients are taken as trial wave functions. As a matter of fact, it is shown that the improvement of the method comes from using better trial wave functions and increasing the order of the Schwinger principle employed.

I. INTRODUCTION

Time dependent quantum systems arise from different branches of atomic physics, such as atomic collisions or strong-laser atom interaction studies. Some important efforts to bring to light the comprehension of these systems beyond the well-known adiabatic or perturbative limits consist on attempting to solve numerically the time-dependent Schrödinger equation governing the system evolution [1–4].

When dealing with atomic collision problems, alternative methods were proposed to cope with atomic excitation (ionization) by fast highly charged ions. For instance, the so called distorted wave methods: symmetric eikonal (SE) [5], the continuum distorted wave - eikonal initial state CDW-EIS [6], and the eikonal-impulse approximation (EIA) [7] were found to be successful to explain experimental results.

On the other hand, the Schwinger variational principle was also able to reproduce experimental data of Fe$^{24+}$ excitation by neutral gases [8, 9]. However, difficulties associated with the calculation of the required second order Born approximation make it hard to achieve a complete assessment of this theory. This, in spite of recent work to include the whole discrete spectrum into the closure calculation [10]. In a different approach, Martin and Salin have recently obtained the second order Born approximation by relating it to the close-coupling calculations. Nevertheless, the accuracy of the two procedures mentioned require some further test, as also admitted by the authors. Moreover, the calculations of variational functionals involving Born terms of higher order than two remain at present a non-tractable evaluation due to the large amount of computational task demanded.

In addition, from a theoretical point of view it is always of interest to test variational principles, such as the Schwinger variational principle, that do not represent minimum principles. The amplitudes obtained with the Schwinger variational principle cannot be employed to bound the exact ones, but just to state that if one is close enough to the scattering wave function, then the resulting transition amplitude differs from the exact one in a second order quantity [10].

In this paper we plan to study the convergence of the variational functional as applied to an exactly solvable model representing a distant collision problem. We require the model to have analytical transition amplitudes in order to generate the whole perturbative series, and also to be able to use it as a benchmark to test the Schwinger variational principles. In section II, different orders of the Schwinger variational transition amplitudes for a time dependent problem are obtained. Section III is devoted to present the model in the context of ion-atom excitation. The results obtained by using the Schwinger functionals are presented in section IV, and a comparison with the corresponding perturbative results as well as with the exact results is performed. Finally, conclusions are drawn in section V. Atomic units will be employed along this work.

II. SCHWINGER VARIATIONAL Amplitudes FOR TIME DEPENDENT PROBLEMS

Let us consider a system where the time dependent Hamiltonian $H$ can be separated into a stationary part $H_0$ characterizing the unperturbed system and a time-dependent interaction potential $V(r, t)$. We consider a one electron atomic hamiltonian

$$H_0 = -\frac{\nabla^2}{2} + V_T(r) \quad (1)$$

where $V_T(r)$ is the atomic interaction.

In what follows, we use the interaction picture, in which the perturbing potential is given by

$$V(t) = \exp(iH_0 t)V(r, t)\exp(-iH_0 t) \quad (2)$$
The dependence on the electron coordinate \( r \) was dropped to distinguish the change from the Schrödinger picture to the Heisenberg picture. Provided that \( V(t \to \pm \infty) \to 0 \), the amplitude for the transition from an initial unperturbed state \( \varphi_i \) to an excited state \( \varphi_f \) is

\[
a_{fi} = \lim_{t \to +\infty} \langle \varphi_f | \psi^+ (t) \rangle = \lim_{t \to -\infty} \langle \psi^- (t) | \varphi_i \rangle
\]  

(3)

where \( \varphi_{i,f} \) are stationary solutions of the unperturbed Schrödinger equation given by

\[
H_0 \ |\varphi_{i,f}\rangle = \varepsilon_{i,f} \ |\varphi_{i,f}\rangle
\]  

(4)

and the scattering wave functions \( \psi^+ (t) \) and \( \psi^- (t) \) satisfy the Lippmann-Schwinger equations

\[
|\psi^+ (t)\rangle = |\varphi_i\rangle - i \int_{-\infty}^{t} dt' V(t') |\psi^+ (t')\rangle \quad (5)
\]

\[
|\psi^- (t)\rangle = |\varphi_f\rangle - i \int_{t}^{+\infty} dt' V(t') |\psi^- (t')\rangle \quad (6)
\]

Note that \( |\psi^- (t)\rangle \) is the advanced scattering state, i.e., \( |\psi^- (t)\rangle \to |\varphi_f\rangle \) as \( t \to -\infty \).

By introducing the Lippman Schwiner equations in Eq. 3 we find the alternative forms for the transition amplitudes

\[
a_{fi} = \delta_{i,f} - i \int_{-\infty}^{\infty} dt \langle \varphi_f | V(t) | \psi^+ (t) \rangle \quad (7)
\]

\[
= \delta_{i,f} - i \int_{-\infty}^{\infty} dt \langle \psi^- (t) | V(t) | \varphi_i \rangle \quad (8)
\]

As it is well known, the Lippmann-Schwinger Eqs. (5) and (6) may be iterated to produce the \( N \)th order of the Born perturbative series

\[
a_{fi}^{(N)} = \delta_{i,f} - i \int_{-\infty}^{\infty} dt_1 \langle \varphi_f | V(t_1) | \varphi_i \rangle + \quad (9)
\]

\[
+ (-i)^2 \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \langle \varphi_f | V(t_1) | V(t_2) | \varphi_i \rangle + ... \quad (9)
\]

\[
+ (-i)^N \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 ... \int_{-\infty}^{t_{N-1}} dt_N \langle \varphi_f | V(t_1) \cdots V(t_N) | \varphi_i \rangle
\]

The order of the Born approximation is given by the number of times the interaction potential is present in the last term of the truncated series.

We associate a Schwinger variational functional with each one of the perturbative expansion orders of the transition amplitude. This task has been done in the context of time independent collisions in reference [11]. For this purpose, we generalize the procedure employed in reference [8]. We rewrite the transition amplitude in the following equivalent ways

\[
a_{fi} = a_{fi}^{(N-2)} + (-i)^{N-1} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 ... \int_{-\infty}^{t_{N-2}} dt_{N-1} \langle \varphi_f | V(t_1) \cdots V(t_N) | \varphi_i \rangle
\]

(10)

\[
a_{fi} = a_{fi}^{(N-2)} + (-i)^{N-1} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 ... \int_{-\infty}^{t_{N-2}} dt_{N-1} \langle \varphi_f | V(t_1) V(t_2) ... V(t_{N-1}) | \psi^+ (t_{N-1}) \rangle
\]

(11)

where \( a_{fi}^{(N-2)} \) denotes the \((N-2)th \) order in the series expansion in Eq. 9.

Other equivalent expressions for the transition amplitude can be generated by replacing \( \varphi_i \) and \( \varphi_f \) in Eqs. 10 and 11 by the forms obtained from Eqs. 7 and 8, respectively:

\[
a_{fi} = a_{fi}^{(N-2)} + (-i)^{N-1} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 ... \int_{-\infty}^{t_{N-2}} dt_{N-1} \langle \varphi_f | V(t_1) V(t_2) ... V(t_{N-1}) | \psi^+ (t_{N-1}) \rangle
\]

(12)

\[
a_{fi} = a_{fi}^{(N-2)} + (-i)^{N-1} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 ... \int_{-\infty}^{t_{N-2}} dt_{N-1} \langle \varphi_f | V(t_1) V(t_2) ... V(t_{N-1}) | \psi^+ (t_{N-1}) \rangle
\]

(13)

Finally, we can generate other alternative expressions for the amplitude by performing Eq. 10 + Eq. 11 - Eq. 12, as follows:

\[
a_{fi} = a_{fi}^{(N-2)} + (-i)^{N-1} \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 ... \int_{-\infty}^{t_{N-2}} dt_{N-1} \langle \varphi_f | V(t_1) V(t_2) ... V(t_{N-1}) | \psi^+ (t_{N-1}) \rangle
\]

(14)

This expression is the Schwinger functional we were looking for. By construction, it gives the exact transition amplitude by using the exact wave functions. Further, it is not difficult to show that this functional is stationary for small variations around the exact wave functions. It may be also demonstrated that when unperturbed wave functions are employed instead of the scattering wave functions, the perturbative transition amplitude to \( n \)th
order is obtained. As an alternative derivation, we might
perform Eq. 10 + Eq. 11 - Eq. 13 to obtain the same
variational functional.

In order to employ the variational principle, we ex-
and the projectile and the electron can be safely rep-
ed. Under this condition, the Coulomb interaction be-
tween the projectile and the electron can be safely rep-
ated functional. Let us consider the collisions of a heavy
harmonic oscillator, whose target potential is given by

\[ V(r, t) = -Z_P \frac{R(t) \cdot r}{R(t)^3} \]

where the dipolar term has been omitted, since it does not
affect the transition probabilities.

The Hamiltonian of the system above corresponds to
the one of a forced isotropic oscillator. This model was
previously employed by Hill and Merzbacher as a
starting point for polarization studies in Coulomb
collisions of charged particles with atoms. The evolution
operator of this time dependent quantum system may be
exactly obtained by separation of variables in the cartes-
ian coordinates \( x, y, z \).

We take the impact parameter \( b \) along the \( y \)-axes, and
the impact velocity \( v \) in the \( z \) direction, \( i.e. \), there are
no perturbations in the \( x \)-direction. Thus, the transi-
tion amplitude to go from the unperturbed initial state
\( | 0, n_y, n_z \rangle \) to a final state \( | m_y, m_z \rangle \), in terms of
one-dimensional transition amplitudes \( a(\alpha, \beta, n, m) \), is given by

\[ a_{\{m\}, \{n\}} = a(\alpha_y, \beta_y, n_y, m_y)a(\alpha_z, \beta_z, n_z, m_z) \]

These amplitudes were obtained in different ways; we
refer the reader to [13] for the analytical calculations.
Here, we just quote the required results. Provided that
the forcing term \( V(q, t) \) is expressed as

\[ V(q, t) = (2w) f(t) \]

the one-dimensional transition amplitudes [13] are given by

\[ a(\alpha, \beta, n, m) = \exp(i\beta - |\alpha|^2/2)(m!)^{\beta}(n!)^{n-m} \times \sum_{j=0}^{m} \frac{(-i\alpha)^j}{j!(n-m+j)!} (n-j)! \]

\[ = \exp(i\beta - |\alpha|^2/2)(m!)^{\beta}(n!)^{n-m} \times \sum_{k=0}^{n} \frac{(-i\alpha)^k}{k!(m-k+j)!} (n-k)! \]

where the magnitudes \( \alpha \) and \( \beta \) are defined as

\[ \alpha = -\int_{-\infty}^{\infty} dt' \exp(iwt') f(t') \]

\[ \beta = -\int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{t_2} dt_1 f(t_1) f(t_2) \sin[w(t_1 - t_2)] \]

In the present case \( \alpha_{y,z} \) have closed forms in terms of
the modified Bessel functions \( K_1 \) and \( K_0 \):

\[ \alpha_y = \frac{2Z_P}{\pi b v^2} a K_1(|a|) \frac{1}{\sqrt{2w}} \]

\[ \alpha_z = \frac{2Z_P}{\pi b v^2} a K_0(|a|) \frac{1}{\sqrt{2w}} \]

where the parameter \( a = wb/v \). On the other hand, the
calculation of \( \beta_{y,z} \) can be reduced to a one-dimensional
integral, resulting in

\[ \beta_y = -\frac{Z_P^2}{\pi b v^2} \int_{-\infty}^{\infty} dy y^2 K_2^2(|y|) \frac{1}{y-a} \]

\[ \beta_z = -\frac{Z_P^2}{\pi b v^2} \int_{-\infty}^{\infty} dy y^2 K_2^2(|y|) \frac{1}{y-a} \]
It is noted that, while $\alpha_{y,z}$ depends linearly on the projectile charge $Z_P$, $\beta_{y,z}$ does quadratically. By expanding the transition amplitude in the parameter $Z_P$, we actually get the perturbative expansion Eq. 9. Doing the same for a generic transition, we obtain easily the matrices $\textbf{V}^{(N-1)}$ and $\textbf{D}^{(N)}$. As the procedure is a long but otherwise straightforward algebraic task, we have employed a commercial code for algebraic and numerical manipulation.

The development of the model we have summarized here was motivated by two main reasons. First, it is exactly solvable so we can obtain both the exact results and the whole perturbation series for any transition. Second, the dipolar approximation yields a good representation of atomic excitation in ion-atom collisions for large values of the projectile charge $Z_P$, the better, the larger $Z_P$. Thus, departures of the model from a real atomic collision system arise only from the target potential.

In the next section, a comparison between the exact transition amplitudes and the different perturbative and Schwinger variational results are presented.

IV. RESULTS AND DISCUSSION

We are interested in representing the non-perturbative region when $Z_P/v$ is greater than one. As we will see, in this case the impact parameter dependent probabilities exhibit a maximum for increasing impact parameters as $Z_P$ is increased. Hence, the dipole approximation is consistent with this feature, namely the importance of the large impact parameters for strong perturbations. A similar behavior is actually evidenced in real atom excitation by fast highly charged ion impact.

We intend to show the performance of the variational principle by studying two case studies in detail. The transition probabilities as a function of the impact parameters for a fixed $Z_P$, and the transition probabilities as a function of the impact parameters for different projectile charges $Z_P$, are presented. We fix the impact velocity in $v = 5$, and the oscillator frequency in $w = 0.5$. It is an easy matter to show that the present problem possesses scaling properties relating the results for different target frequencies $w$, and also for different velocities.

We study excitation from the ground state $|0s\rangle$ to the first excited states $|1p_0\rangle$ and $|1p_1\rangle$. We also discuss results for the elastic probabilities. The final states with well defined angular momentum can be obtained by using straightforward and well known transformation rules in terms of the one-dimensional transition amplitudes $a(\alpha, \beta, n, m)$.

A. Fixed projectile charge as a function of the impact parameter

Here, we analyze the case where the projectile charge is fixed ($Z_P = 12$), and the transition probabilities determined as a function of the impact parameter. This is the normal procedure in order to obtain a total cross section. The transition to a strong perturbation regime for a fixed $Z_P$ is accounted for by decreasing the impact parameter. We are interested in the region of impact parameter where the dipolar hypothesis remains valid, say $b > 2$. Indeed, as will be deduced below, this range is the one that mostly contributes to the total cross section as $Z_P$ becomes larger than $v$ in atomic units. The calculations performed with the Born and with the Schwinger variational functional of order $N$ are denoted by $B_N$ and $S_N$, respectively. For the trial initial and final wave functions we consider a basis set of the 16 lower energies states.

First transition probabilities for $0s \rightarrow 1p_0$ (figure 1) and $0s \rightarrow 1p_1$ (figure 2) as a function of the impact parameter $b$ are analyzed. In figures 1a and 2a results obtained with the Born series $B_2$, $B_4$ and $B_6$ are displayed. It may be observed that the Born expansion remains close to the exact results for large $b$. For the Born results of order 6, the results agree for $b > 5$. For lower orders of the Born series, the exact results are only well represented for higher impact parameters. This behavior delimits convergence properties of the Born series.

On the other hand, the corresponding results obtained with the associated Schwinger functionals are shown in
FIG. 2. Transition probabilities for the \( |0s\rangle \rightarrow |1p_1\rangle \) transition as a function of the impact parameter for \( Z_P = 12 \), \( v = 5 \), and \( w = 0.5 \). (a) Born approximation of order \( n \), \( B_n \), (b) Schwinger variational approximation of order \( n \), \( S_n \) with 16 basis set expansion. Solid line curves correspond to exact model results.

figures 1b and 2b. The improvement over the Born series is noteworthy. Even with the Schwinger functional of order 2 (S2), the qualitative behavior is fairly improved. Notably, the S6 results are in good agreement with the exact ones for \( b > 2.5 \). The Schwinger functionals are convergent as the order is increased, although for small impact parameters the probabilities are largely overestimated by the higher orders. This is a well known problem with variationally obtained magnitudes when the trial wave functions are not reasonably close to the exact ones.

Briefly, as the order of both the Schwinger and the Born amplitudes increases the results approaches the exact ones. However, as expected, Schwinger variational calculation are a good improve over Born ones.

B. Probabilities for different projectile charges

In the results obtained for different projectile charges as a function of the impact parameter, the transition to a strong perturbation regime is taken into account by increasing the projectile charge. This analysis is motivated by previous ideas [3] concerning the behavior of the transition amplitudes for large values of the projectile charges. First Born approximations give a simple \( Z_P^2 \) scaling for the transition probabilities, i.e., probabilities do increase in a monotonous way with the projectile charge.

Transition probabilities for \( 0s \rightarrow 1p_0 \) (figure 3) and \( 0s \rightarrow 1p_1 \) (figure 4) transitions as a function of the impact parameter \( b \) are show again. Four values of the projectile charge: 2, 6, 12 and 20 are considered. Now, we focus on a comparison between the results Born results B6 (figure 3a an 4a ) with the Schwinger S6 ones (figure 3b and 4b). Probabilities show maxima at increasing impact parameter as the projectile charge is increased, following roughly a \( \sqrt{Z_P} \) law. Thus, for higher charges the distant collisions yield the larger transition probabilities. Therefore distant collisions contributes the most to total cross sections. Probabilities obtained with the simplest B6 agree with the exact only beyond the maxima curves. For \( 0s \rightarrow 1p_1 \) transition not even the maxima are displayed by this high order Born approximation calculations. In the case of the S6 results, the agreement with the exact curves is both qualitative and quantitative for \( b > 4 \) in the case of \( Z_P = 20 \), and for \( b > 1 \) in the case...
of $Z_P = 2$. For lower values of $b$, the Schwinger results break down, and probabilities are again largely overestimated. However as mentioned before these impact parameters range are not relevant total cross sections.

C. Convergence with the basis expansion set

Finally, results obtained with the Schwinger functional of order 6, but for different sizes of basis sets, are displayed in figure 5. The elastic probabilities are shown. The S6 fails when only the initial and final states are included in the basis set. In this case, the same results as the Born approximation of order 2 are obtained. For elastic probabilities and accounting for selection rules, the results with a single state basis set gives unity for any impact parameter. Moderate to large basis states are in good agreement with the exact results. The limit case of a very large basis set is well represented by using 16 states. No further improvement is obtained by increasing the basis set over this size.

The ultimate reason for this kind flat behavior is that the coefficients in the trial wave functions are required to be independent of time. If the coefficients would be allowed to have a time dependence the description would become accurate for any impact parameter as the basis set increases.

![FIG. 5. Probabilities for the $|0s\rangle \rightarrow |0s\rangle$ elastic process as a function of the impact parameter for $Z_P = 12$, $v = 5$, and $w = 0.5$. Schwinger variational approximation of order 6 (S6) for different number of states in the basis set. Solid curves are exact results.](image)

V. CONCLUSIONS

Martin and Salin [4] have reported some doubts about the convergence properties of the Born series in ion-atom excitation problems based on close-coupling calculations. From the present work, we conclude that convergence of the Born series is assured for large impact parameters. As the Born order is increased, convergence for decreasing impact parameters is obtained. It looks like that for large enough Born series order the minimum impact parameter that is well described may be pushed down even more.

The improvement obtained by using the Schwinger functionals arises from increasing both, the order and the basis set size. In this work, we have shown the superiority of the variational calculations as compared with Born results of the same order. We remark that, once the Schwinger convergence fails, the probabilities are even worse than those obtained with the Born series. The performance of the Schwinger functional depends critically on the accuracy of the Born terms. This is particularly true for large projectile charges because of the multiplication of the $N$-order term by $Z_P^N$. Whether this level of convergence of the Schwinger variational amplitudes may be obtained in the real ion-atom collision problem is an open question. However, this work may encourage further research to address this line.

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