Time-Independent Wave-Packet Forms of Schrödinger and Lippmann-Schwinger Equations

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Time-independent wave-packet forms of the Schrödinger equation (TIWSE) and Lippmann-Schwinger equation (TIWLSE) have been derived by a partial time-to-energy Fourier transform of L^2 wave-packet solutions to the time-dependent Schrödinger equation. The new equations retain the initial wave packet $\chi(t_0)$ as a "universal source" of scattered waves, which applies for *all* collision energies E contained in the initial wave packet. The relationship between the solution $\Psi_{t_0}(E)$ of the TIWSE or TIWLSE and the scattering solution $\Psi^{(+)}(E)$ of the standard time-independent Lippmann-Schwinger or Schrödinger equation is given and the method illustrated by a computational application.

The time-independent Lippmann-Schwinger equation (TILSE) is fundamental in formal scattering theory since, unlike the time-independent Schrödinger equation (TISE), it explicitly contains the boundary conditions ensuring a physically correct wave function [1]. Definite energy scattering solutions manifest less convenient properties than bound states. In particular, definite energy scattering states correspond to cases where the colliding partners separate arbitrarily far. Thus, the wave function does not vanish at large separations and does not belong to Hilbert space, i.e., it is not "normalizable" ("L^2"). It is well known that the TILSE rigorously comes from solving the time-dependent Schrödinger equation (TDSE) [1]. Time-dependent solutions *are* L^2 functions, constructed as superpositions (wave packets) of the non-L^2 definite energy states. A rigorous, wave-packet derivation of the TILSE has been given in considerable detail in the classic work of Golberger and Watson [1]. The TILSE is

$$\Psi_k^{(+)}(E) = \phi_k(E) + \frac{1}{E - H + i\epsilon} V\phi_k(E), \tag{1}$$

where $\Psi_k^{(+)}(E)$ is the causal or outgoing scattered wave solution, H is the full Hamiltonian composed of the sum of an unperturbed piece K describing the well-separated projectile and target, and a perturbation V responsible for the scattering, ϵ is a positive parameter ensuring the causal boundary condition on the scattered waves, and $\phi_k(E)$ is the solution of the free TISE,

$$(E - K)\phi_k(E) = 0. \tag{2}$$

It is sufficient and convenient here to treat a one-dimensional problem; $\phi_k(E)$ is simultaneously an eigenstate of linear momentum ($= \hbar k$) and energy E ($= \hbar^2 k^2/2m$). Note that in three dimensions, k is a vector. In the 1D case, its vector nature is reflected in the occurrence of both positive *and* negative values, so there is a twofold degeneracy. The scattered wave portion of $\Psi_k^+(E)$ is

$$\Psi_{SW}^{(+)}(E) = \frac{1}{E - H + i\epsilon} V\phi(E). \tag{3}$$

We close this summary by noting the properties of $\Psi_{SW}^{(+)}(E)$, based on Eq. (3). Most important is the fact that the scattered wave source $V\phi_k(E)$ depends on energy E. Thus the action of $(E - H + i\epsilon)^{-1}$ must be completely recalculated at *every* energy, no matter how one chooses to compute the scattered wave [2-6], and a large portion of the work in solving Eqs. (1) and (3) must be repeated at every energy.

It would be enormously useful to have a TISE or TILSE with a *universal* source replacing $V\phi(E)$; i.e., a source of scattered waves independent of the energies of interest. Here we report the derivation of a new inhomogeneous TISE, and concomitant LS-like equation which does have a universal source function, and more importantly, explicate the relationship of the new to the old equations and solutions. The new equations, like the standard TILSE, result from time-dependent (wave-packet) quantum dynamics; they can be viewed as *time-independent wave-packet Schrödinger* and *wave-packet Lippmann-Schwinger* equations (TIWSE and TIWLSE). The universal source is the initial wave packet [a superposition of $\phi(k)$'s with different k's or energies], so that the same source applied for any energy contained in the initial wave packet. To simplify the analysis, we consider initial wave packets with momenta pointing only toward the target. The initial wave packet is positioned to the left of the target, so only positive semidefinite momenta are employed. Below, we analyze the solution to these new equations and compare them to those of the standard equations. We also give results from an example application of the new equations.

We begin with the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \chi}{\partial t} = H\chi, \tag{4}$$

where $\chi(t)$ is a localized, L^2 function. This equation is solved by an integrating factor to yield

$$\chi(t) = \exp(-iH[t - t_0]/\hbar)\chi(t_0), \tag{5}$$

where t_0 is any time *prior* to the overlap of the wave

packet with the target. [To verify that $\chi(t)$ is a solution, simply substitute it into Eq. (4).] The essential step in deriving the TIWLSE is to do a partial time-to-energy Fourier transform of $\chi(t)$. We *define* the function Ψ_{t_0} by

$$\Psi_{t_0}(E) = \frac{1}{2\pi\hbar} \int_{t_0}^{\infty} dt\, e^{iE(t-t_0)/\hbar}\chi(t),\qquad (6)$$

and because $\chi(t)$ is an L^2 wave packet, the integral converges as written. One can carry out the time integral *formally* by inserting the usual convergence factor, $\exp[-\epsilon(t-t_0)]$. The subscript t_0 implies that the *time-independent* wave function $\Psi_{t_0}(E)$ may depend on the initial time t_0. Figure 1 shows how space is divided into three regions by the initial, localized wave packet. The packet $\chi(t)$ for $t \geq t_0$, while remaining L^2, can spread out in *all* regions of configuration space, depending on the value of t. However, $\chi(t)$ for t sufficiently less than t_0 will be non-negligible *only* in region III, assuming that

$$\chi(t_0|x) = \int_0^{\infty} dk'\, A(k')e^{ik'x}\qquad (7)$$

(i.e., that all the components of the initial wave packet are moving toward the region of the potential at $t = t_0$, and that at time t_0 the packet is non-negligible only in region II).

We begin by evaluating Eq. (6) in region I [to the right of $\chi(t_0|x)$]. Combining Eqs. (5) and (6), and integrating over t analytically, we obtain

$$\Psi_{t_0}(E) = \frac{1}{2\pi\hbar} \int_{t_0}^{\infty} dt\, e^{i(E^+ - H)(t-t_0)/\hbar}\chi(t_0)\qquad (8)$$

or

$$\Psi_{t_0}(E) = \frac{1}{2\pi i} e^{-i(E^+ - H)t_0/\hbar} \frac{1}{(E - H + i\epsilon)}$$
$$\times e^{i(E - H + i\epsilon)t/\hbar}\big|_{t=t_0}^{\infty}\chi(t_0),\qquad (9)$$

where $E^+ = E + i\epsilon, \epsilon > 0$. The upper limit yields zero and the lower limit yields

$$\Psi_{t_0}(E) = \frac{i}{2\pi} \frac{1}{(E - H + i\epsilon)}\chi(t_0).\qquad (10)$$

Using the LSE for the full Green's operator in terms of the free Green's operator $(E - K + i\epsilon)^{-1}$,

$$\frac{1}{E - H + i\epsilon} = \frac{1}{E - K + i\epsilon} + \frac{1}{E - H + i\epsilon} V \frac{1}{E - K + i\epsilon},\qquad (11)$$

where K is the kinetic energy operator, along with Eq. (7), we write

$$\Psi_{t_0}(E|x)$$
$$= \frac{i}{2\pi} \int_0^{\infty} dk'\, A(k') \frac{e^{ik'x} + (E - H + i\epsilon)^{-1}Ve^{ik'x}}{E - E' + i\epsilon}.\qquad (12)$$

Here we have used the fact that

$$\frac{1}{E - K + i\epsilon} e^{ik'x} = \frac{1}{E - E' + i\epsilon} e^{ik'x}\qquad (13)$$

since

$$Ke^{ik'x} = \frac{(\hbar k')^2}{2m} e^{ik'x} = E'e^{ik'x}.\qquad (14)$$

But by Eq. (1), we can write Eq. (12) as

$$\Psi_{t_0}(E|x) = \frac{i}{2\pi} \int_0^{\infty} dk' \frac{A(k')}{E - E' + i\epsilon}\Psi_k^{(+)}(E'|x)\qquad (15)$$

and by changing the integration variable from k' to E' and using the Cauchy residue theorem, obtain

$$\Psi_{t_0}(E|x) = \frac{mA(k)}{\hbar^2 k}\Psi_k^{(+)}(E|x),\quad x \in \text{region I},\qquad (16)$$

with $E = \hbar^2 k^2/2m$.

Now we note that we could also have written the right-hand side of Eq. (8) as

$$\int_{t_0}^{\infty} dt\, e^{(E-H)(t-t_0)/\hbar}\chi(t_0)$$
$$\equiv \left[\int_{-\infty}^{\infty} dt - \int_{-\infty}^{t_0} dt\right] e^{i(E-H)(t-t_0)/\hbar}\chi(t_0),\qquad (17)$$

and note that, in region I, the second term is zero. This is because it corresponds physically to evolving the packet backward in time, and since $\chi(t_0)$ has only positive semidefinite momenta, the packet must move further away from region I. However, this shows that

$$\frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\, e^{i(E-H)(t-t_0)/\hbar}\chi(t_0) = \frac{mA(k)}{\hbar^2 k}\Psi_k^{(+)}(E),\qquad (18)$$
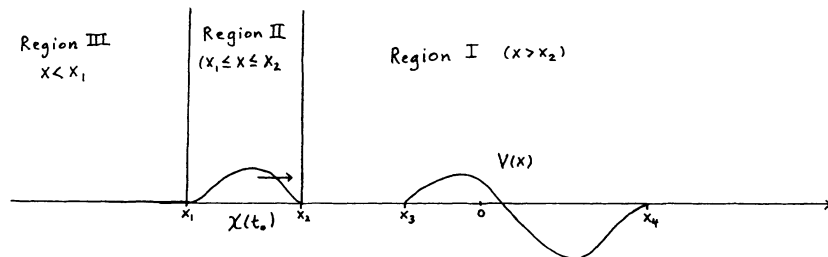

FIG. 1. Regions I, II, and III are depicted. Region I includes all x values beyond the leading edge of the initial wave packet [which is taken to *not* overlap the target or potential, $V(x)$]. Region III includes all x values behind the trailing edge of the initial wave packet. Region II is that where $\chi(t_0)$ is significantly different from zero.

which holds not only in region I, but everywhere. [The above can also be proved using the fact that the initial wave packet can be expressed as a superposition of the LS states with the *same* expansion coefficients $A(k)$ as occur in the plane wave superposition, make use of the fact that these LS states are eigenstates of the full Hamiltonian H, and then doing the time integration using a well known representation of the Dirac delta function.]

Finally, we use Eqs. (17) and (18) to evaluate $\Psi_{t_0}(E|x)$ in region III as

$$\Psi_{t_0}(E|x) = \frac{mA(k)}{\hbar^2 k}\Psi^{(+)}(E|x) - \frac{1}{2\pi\hbar}\int_{-\infty}^{t_0} dt\, e^{i(E-H)(t-t_0)/\hbar}\chi(t_0), \quad x \in \text{region III}. \tag{19}$$

Evaluating the integral over t formally using the convergence factor $\exp(\epsilon[t-t_0]/\hbar)$, we have

$$-\int_{-\infty}^{t_0} dt\, e^{i(E-H-i\epsilon)(t-t_0)/\hbar}\chi(t_0) = -\frac{1}{2\pi i}e^{-i(E-H-i\epsilon)t_0/\hbar}\frac{1}{E-H-i\epsilon}e^{i(E-H-i\epsilon)t/\hbar}\big|_{t\to-\infty}^{t=t_0}\chi(t_0). \tag{20}$$

The lower limit gives zero and the upper limit yields

$$-\int_{-\infty}^{t_0} dt\, e^{i(E-H)(t-t_0)/\hbar}\chi(t_0) = \frac{i}{2\pi(E-H-i\epsilon)}\chi(t_0), \quad x \in \text{region III}. \tag{21}$$

But in region III, H equals K (the potential is zero there) and using Eq. (7) we write in this region

$$-\int_{-\infty}^{t_0} dt\, e^{i(E-H)(t-t_0)/\hbar}\chi(t_0) = \frac{i}{2\pi}\int_0^\infty dk' \frac{A(k')e^{ik'x}}{E-(\hbar k')^2/2m-i\epsilon}. \tag{22}$$

This is closed with a counterclockwise contour and by the Cauchy residue theorem yields

$$-\int_{-\infty}^{t_0} dt\, e^{i(E-H)(t-t_0)/\hbar}\chi(t_0) = -\frac{mA(k)}{\hbar^2 k}e^{ikx}, \tag{23}$$

so that in region III we have

$$\Psi_{t_0}(E|x) = [mA(k)/\hbar^2 k][\Psi_k^{(+)}(E|x) - e^{ikx}], \tag{24}$$

which just involves the *scattered wave*. The dependence of $\Psi_{t_0}(E|x)$ on t_0 is strictly only in the precise extent of regions I, II, and III, and this is controlled by $\chi(t_0)$. Within regions I and III, $\Psi_{t_0}(E|x)$ is given by Eqs. (16) and (24), respectively, and is thus independent of "t_0" within these regions. In region II, which disjoins regions
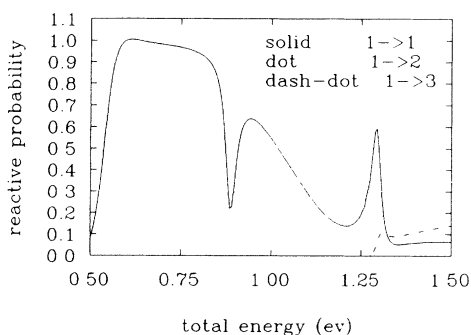

FIG. 2. The reactive transition probabilities (for transfer of the central H atom) are plotted versus total energy in electron-volts (eV). The solid curve denotes $H + H_2(a,v=0) \rightarrow H_2(\beta,v'=0) + H$, where the reactant arrangement is labeled a and the product arrangement β. The dotted curve is for the product molecule in the $v'=1$ (first excited) vibrational state, and the dash-dotted curve is for the product molecule in the $v'=2$ (second excited) vibrational state. The results agree to graphical accuracy with those of Bondi and Connor [11].

I and III, $\Psi_{t_0}(E)$ makes a continuous transition between its functional forms in regions I and III. As $t_0 \rightarrow -\infty$, region I includes *all* of configuration space and $\Psi_{t_0}(E)$ is proportional to $\Psi_k^{(+)}(E)$ everywhere.

We have applied the new formalism and analysis to a realistic model for rearrangement scattering of a hydrogen atom with a H_2 diatomic molecule, constrained to a line. Both nonreactive and reactive scattering are allowed. The system is well studied and, at certain energies long-lived resonance complexes are formed [7]. We follow earlier investigations in using the "LSTH" potential surface for the calculations [8]. The action of the full Green's function $(E-H+i\epsilon)^{-1}$ on the initial packet, $\chi(t_0)$, in Eq. (10) is evaluated as a sum of Chebychev polynomials according to [9,10]

$$\Psi_{t_0}^{(N)}(E) = \sum_{n=0}^N a_n(E,\bar{H},\Delta H)T_n(H')\chi(t_0), \tag{25}$$
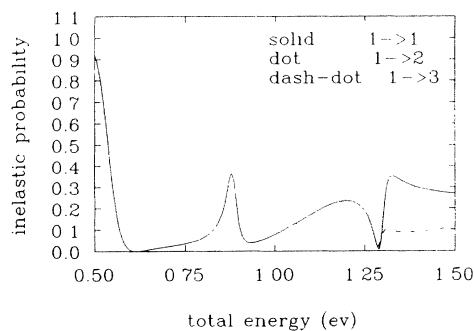
where

FIG. 3. As in Fig. 2, except that the process is nonreactive. Thus, the final molecule can be in the $v'=0,1,2$ states, but no exchange of atoms has occurred.

$$H' = (H - \bar{H})/\Delta H \,, \tag{26}$$

$$\bar{H} = (H_{max} + H_{min})/2 \,, \tag{27}$$

$$\Delta H = (H_{max} - H_{min})/2 \,, \tag{28}$$

$$a_n(E,\bar{H},\Delta H) = \frac{(2 - \delta_{n_0})\exp(-iEt_0/\hbar)[E - \bar{H} - i\sqrt{(\Delta H)^2 - (E - \bar{H})^2}]^n}{2\pi(\Delta H)^n\sqrt{(\Delta H)^2 - (E - \bar{H})^2}} \,, \tag{29}$$

with H_{max} and H_{min} the maximum and minimum eigenvalues of H [8,11]. *All* the energy dependence resides in the purely scalar factors $a_n(E,\bar{H},\Delta H)$ so that once the "basis vectors," $T_n(H')\chi(t_0)$, $n = 0,1,\ldots,N$ are known, constructing solutions for any energies contained in $\chi(t_0)$ involves very little extra work. $\Psi_{t_0}(E)$ is approximated by a sequence of normalizable functions $\Psi_{t_0}^{(N)}(E)$ with N chosen so that the normalizable $\Psi_{t_0}^{(N)}(E)$ coincides with the non-normalizable $\Psi_{t_0}(E)$ only in the region including and surrounding the potential.

In Figs. 2 and 3 we give results for reactive and non-reactive transitions over a range of energies. These results were obtained from *a single* initial Gaussian wave packet for translation of the incident H atom times the ground vibrational state. The results agree (to graphical accuracy) with earlier solution of the TISE [11].

The TIWLSE approach corresponds to a purely spatial wave-packet propagation versus the temporal-spatial wave-packet propagation of standard time-dependent quantum mechanics. Because of universal source and the simple relation of the new solution to the TILS solution results for many energies are obtained from a single spatial propagation using an initial-value-like computational approach. This transfers to time-independent quantum scattering the advantages possessed by wave packet methods [12,13].

Finally, we note that although the partial time-to-energy transform leads to a new formalism for time-independent scattering theory, an analogous transform has long been used in the treatment of the quantum mechanical Liouville or von Neumann equation in statistical mechanics [14].

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