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Perturbative, acausal effects in ultracold non-crossing atomic collisions

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Abstract

Coupled second-order quantal wave equations are considered for a non-crossing atomic collision. They are reduced to *exactly* equivalent first-order equations. The semiclassical approximation transforms these equations into generalized projectile–target time-dependent interaction impact parameter equations. We show that in the suggested approach acausal, cybernetic effects are observed when terms propagate in the acausal (negative to positive time) direction. We summarize the results obtained and illustrate these effects in the quantal first Born approximation.

1. Introduction

In the quantum mechanics of atomic collisions, the time-dependent Schrödinger equation (TDSE) is causal with respect to the time behaviour. This includes the impact-parameter treatment of ion–atom collisions. This latter treatment assumes that the relative motion of the nuclei is described *a priori* by a classical trajectory, for instance, a straight line or a Coulomb curved line. Nevertheless, the behaviour of the electrons is described by quantum mechanics.

However, there is a major difference, depending on whether we consider the general causal TDSE or the impact-parameter treatment. In the fully quantal TDSE describing three particles (an electron colliding with a one-electron atom, or a proton or other heavy particle colliding with a similar atom), the time dependence may be removed immediately by a gauge transformation: factoring out $\exp(-\mathrm{i}Et/\hbar)$ where E is the total energy. This is because we may assume that, in these three-body collisions, all three two-body interactions are time independent and may be described using the time-independent (or stationary) Schrödinger equation. Note that we are excluding time-dependent external fields in these statements. To continue with the

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major difference, consider further the impact-parameter treatment. The classical treatment of the relative motion of the collidants means that a gauge transformation $\exp\left(-\frac{\mathrm{i}}{\hbar}\int_0^t \frac{z_P z_T}{R'}\,\mathrm{d}t'\right)$ removes the internuclear interaction (here the charge of the bare projectile is z_P and of the target nucleus is z_T and the internuclear distance is R, which may be taken as $\sqrt{\rho^2 + v^2t^2}$ in the straight-line case, with impact parameter ρ, time t and impact velocity v). However, the price one pays is that the TDSE must be used since the two other two-body interactions are time dependent. Nevertheless, a major advantage is that the variational principle (second-order-in-space, first-order-in-time Jacobi–Euler–Lagrange–Sil) leads to coupled first-order ordinary differential equations in the impact-parameter treatment (Sil 1960). In contrast, in the time-independent Schrödinger equation quantal wave treatment the variational principle (second-order-in-space Jacobi–Euler–Lagrange–Kohn) leads to coupled second-order ordinary differential equations, by separating the variables and following a partial-wave analysis (Mott and Massey 1965).

Equally well, it is known that these wave and impact-parameter treatments of an ion–atom collision are effectively equivalent in the first-Born perturbation approximation, under rather minimal assumptions, notably a large reduced mass of the projectile and the nuclear target (Crothers and Holt 1966). Thus it should come as no surprise that the so-called time-independent treatment actually does involve an underlying time dependence which is equivalent to the impact-parameter time. As we shall demonstrate in what follows, this underlying time involves acausal effects, as viewed from the impact-parameter treatment. This will be interpreted as a generalized impact parameter treatment.

When we use the word 'semiclassical' we shall be referring to the Jeffreys–Wentzel–Kramers–Brillouin (JWKB) approximation, rather than the impact-parameter method for which the relative motion of the heavy particles is described classically and the electrons quantally. In some countries, the impact-parameter method is described as semiclassical!

In Bichoutskaia *et al* (2002) we introduce in the notation of Mott and Massey (1965, chapter XIII, equations (10), (11)) the atomic collision problem in the two-state approximation described in terms of two coupled radial Schrödinger equations:

$$\begin{aligned}
\frac{\mathrm{d}^2G_{0l}}{\mathrm{d}r^2} + \left(k_0^2 - \frac{l(l+1)}{r^2} - U_{00}(r)\right)G_{0l} &= U_{01}G_{1l}, \\
\frac{\mathrm{d}^2G_{1l}}{\mathrm{d}r^2} + \left(k_1^2 - \frac{l(l+1)}{r^2} - U_{11}(r)\right)G_{1l} &= U_{10}G_{0l}
\end{aligned} \tag{1}$$

for each value of the total angular-momentum quantum number l. These may be derived from a two-state ansatz using second-order Euler–Lagrange variational theory (for the latest development in variational principles for second-order differential equations, see Grifone and Muzsnay (2000)). In (1), $U_{10} = U_{01} \equiv 2MV_{01}/\hbar^2$ is the coupling matrix element where V_{01} is the offdiagonal interaction matrix element for the colliding systems and the wavenumbers $k_j = k_j(\infty)$, $j = 0, 1$, are related to the relative velocity $v_j(\infty)$ of separated atoms in the state j as

$$k_j = \frac{Mv_j(\infty)}{\hbar}, \tag{2}$$

where M is the reduced mass; r is the projectile–target separation. The distortion of state i (0 or 1) due to interaction with the state j ($j \neq i$) is given by the diagonal matrix element $U_{ii}(r)$. The channel wavefunctions G_{jl} are regular at the origin,

$$G_{0l}(0) = G_{1l}(0) = 0, \tag{3}$$

and satisfy, as $r \to \infty$, the boundary conditions

$$\begin{aligned} G_{0l}(r \to \infty) &= \mathrm{i}^l \sin(k_0(\infty)r - l\pi/2) + \alpha_l \exp(\mathrm{i}k_0(\infty)r), \\ G_{1l}(r \to \infty) &= \beta_l \exp(\mathrm{i}k_1(\infty)r) \end{aligned} \tag{4}$$

if the colliding entities are prepared in the state 0, where α_l and β_l are constants (independent of r). The constant β_l is the inelastic amplitude related to the S-matrix element $\mathcal{S}_{01}^l$ by

$$\mathcal{S}_{01}^l = 2\mathrm{i}\sqrt{\frac{k_1(\infty)}{k_0(\infty)}}\beta_l$$

and the (partial) transition probability P_l is given traditionally by

$$P_l = \frac{4k_1^2(\infty)}{k_0^2(\infty)}|\beta_l|^2 = \frac{k_1(\infty)}{k_0(\infty)}|\mathcal{S}_{01}^l|^2. \tag{5}$$

2. Generalized impact-parameter treatment

The two coupled channel equations (1) can be transformed into four first-order ones (Bates and Crothers (1970), to be referred to as (I)) by introducing the uncoupled channel wavefunctions $S_{jl}^{\pm}$ (solutions of equation (1) without the right-hand side) containing at $r \to \infty$ only the outgoing and incoming waves, respectively:

$$S_{jl}^{\pm}(r) \approx k_j^{-1/2} \exp\left(\pm\mathrm{i}\left(k_j r - \frac{l\pi}{2}\right)\right). \tag{6}$$

Expanding the solutions $G_{jl}(r)$ in the form

$$G_{jl}(r) = \alpha_{jl}^{+}(r)S_{jl}^{+}(r) + \alpha_{jl}^{-}(r)S_{jl}^{-}(r) \tag{7}$$

leads (I) to the following exact equations for the coefficient functions $\alpha_{jl}^{\pm}$:

$$\begin{aligned} \alpha_{0l}^{+'} &= -\tfrac{1}{2}\mathrm{i}U_{01}S_{0l}^{-}(\alpha_{1l}^{+}S_{1l}^{+} + \alpha_{1l}^{-}S_{1l}^{-}), \\ \alpha_{0l}^{-'} &= +\tfrac{1}{2}\mathrm{i}U_{01}S_{0l}^{+}(\alpha_{1l}^{+}S_{1l}^{+} + \alpha_{1l}^{-}S_{1l}^{-}), \\ \alpha_{1l}^{+'} &= -\tfrac{1}{2}\mathrm{i}U_{10}S_{1l}^{-}(\alpha_{0l}^{+}S_{0l}^{+} + \alpha_{0l}^{-}S_{0l}^{-}), \\ \alpha_{1l}^{-'} &= +\tfrac{1}{2}\mathrm{i}U_{10}S_{1l}^{+}(\alpha_{0l}^{+}S_{0l}^{+} + \alpha_{0l}^{-}S_{0l}^{-}). \end{aligned} \tag{8}$$

In terms of $\alpha_{jl}^{\pm}$ the boundary conditions (3), (4) may now be written as

$$\begin{aligned} &\alpha_{0l}^{-}(\infty) = \tfrac{1}{2}k_0^{1/2}(\infty), \qquad && \alpha_{1l}^{-}(\infty) = 0, \\ &\alpha_{jl}^{+}(0) + \alpha_{jl}^{-}(0) = 0 && (j = 0, 1). \end{aligned} \tag{9}$$

The advantage of representation (8) is that the properties of the uncoupled system enter the equations through $S_{jl}^{\pm}(r)$. This makes (8) a convenient basis for semiclassical treatment, as one only needs to replace the $S_{jl}^{\pm}(r)$ by their semiclassical asymptotes.

Thus far no approximation has been made and we have reduced two coupled second-order differential equations to four coupled first-order equations by a method which is essentially equivalent to the well known variation-of-parameters method.

For simplicity we consider the non-crossing model in which ϵ_0 and ϵ_1 are the separated-atom eigenenergies:

$$U_{00} = U_{11} = 0 \tag{10}$$

and define

$$W(r) \equiv \frac{V_{01}(r)}{v}. \tag{11}$$

In the non-crossing case $k_0^2 - U_{00}(r) \neq k_1^2 - U_{11}(r)$ for all r, whereas for pseudo- or avoided-crossings there exists at least one r for which the inequality becomes an equality. Following (I) we introduce the diabatic JWKB semiclassical approximation (with Langer correction)

$$S_{jl}^{\pm}(r) = k_j^{-1/2} \exp\left(\pm \mathrm{i}\left(\frac{\pi}{4} + k_j\left(r - \frac{\pi}{2}\rho_j\right)\right)\right) \tag{12}$$

which holds asymptotically and which includes an extra $\pm\frac{\mathrm{i}\pi}{4}$, compared to equation (6) (and with an eye on the connection formula at the classical turning point), and where we have impact parameters given by

$$\rho_0 k_0 = l + \tfrac{1}{2} = \rho_1 k_1, \tag{13}$$

and

$$\rho^2 = \rho_0 \rho_1. \tag{14}$$

In contrast to the adiabatic model of slowly varying behaviour for which we could diagonalize the matrix $\boldsymbol{V}$ ($V_{01} \neq 0$), in the diabatic treatment we neglect W (i.e. V_{01}, U_{01}, U_{10}) and solve the remaining homogeneous equations (1) to obtain $S_{jl}^{\pm}(r)$ of (12). We define, with $c_0(-\infty) = 1$ and $c_1(-\infty) = 0$, and suppressing l

$$c_j(z) = \begin{cases} +\alpha_{jl}^{+}(|z|) & (z \geqslant 0) \\ -\alpha_{jl}^{-}(|z|) & (z \leqslant 0) \end{cases} \tag{15}$$

where the path length z satisfies

$$|z| = v|t| = \sqrt{r^2 - \rho^2}. \tag{16}$$

The remnant distortion (Bates 1961) is given by

$$\left.\begin{matrix}\mu \\ \gamma\end{matrix}\right\} = \left[k_0|z| - \left(l + \frac{1}{2}\right)\frac{\pi}{2} + \frac{\pi}{4}\right] \mp \left[k_1|z| - \left(l + \frac{1}{2}\right)\frac{\pi}{2} + \frac{\pi}{4}\right], \tag{17}$$

(upper sign for μ being $+-$ or $-+$ distortion, lower sign for γ being $++$ or $--$ distortion), so that

$$\mu = (k_0 - k_1)|z| \tag{18}$$

$$\gamma = (k_0 + k_1)|z| - l\pi. \tag{19}$$

Treating W as slowly varying and invoking the Gans–Jeffreys connection formula based on (9), and by the substitution of equations (12) and (15), equations (8) may now be rewritten in the classically allowed region (cf 'forbidden' region in Coveney *et al* (1985)) as the generalized impact-parameter equations

$$\frac{\mathrm{i}\,\mathrm{d}c_0(z)}{\mathrm{d}z} = W[c_1(z)\mathrm{e}^{\mp\mathrm{i}\mu} - c_1(-z)\mathrm{e}^{\mp\mathrm{i}\gamma}] \tag{20}$$

$$\frac{\mathrm{i}\,\mathrm{d}c_1(z)}{\mathrm{d}z} = W[c_0(z)\mathrm{e}^{\pm\mathrm{i}\mu} - c_0(-z)\mathrm{e}^{\mp\mathrm{i}\gamma}] \tag{21}$$

upper or lower sign according to $z > 0$ or $z < 0$. The second terms in the RHS square brackets in equations (20) and (21) may be regarded as acausal because for negative z they have not yet been reached by the classical trajectory. These acausal terms come from the $S_{0l}^{-}S_{1l}^{-}$ and $S_{0l}^{+}S_{1l}^{+}$ terms in (8). The difference between equations (20) and (21) and the standard impact-parameter treatment (Bates 1961) lies entirely in the $c_j(-z)$ terms. The normal argument in ion–atom collisions is that $\mathrm{e}^{\pm\mathrm{i}\gamma}$ averages out at zero for large γ. Mathematically, we have $c_j(-z)$ as against $c_j(z)$ and the terms which run backwards in time do occur. We call them acausal terms in contrast with causal processes of movement forward in time. It follows that the exact relations hold, namely

$$\frac{\mathrm{d}c_0(-z)}{\mathrm{d}z} = \exp(\pm\mathrm{i}(\mu+\gamma))\frac{\mathrm{d}c_0(z)}{\mathrm{d}z} \tag{22}$$

$$\frac{\mathrm{d}c_1(-z)}{\mathrm{d}z} = \exp(\pm\mathrm{i}(\gamma-\mu))\frac{\mathrm{d}c_1(z)}{\mathrm{d}z}. \tag{23}$$

By inspection, these relations embrace cybernetic (or feedback) effects. To wit, if $z > 0$, then earlier amplitudes (or rather, their rates of change) are given in terms of the later amplitudes. Viewed from the impact-parameter trajectory, the absence of acausal terms in equations (20) and (21) would negate relations (22) and (23).

3. Perturbation theory

We now apply double-perturbation theory (Born approximation) which invokes $W \ll 1$, which implies $c_1(+\infty) \approx 0$ and neglecting the oscillatory acausal term in (21), we obtain

$$\frac{\mathrm{i}\mathrm{d}c_1(z)}{\mathrm{d}z} \approx W\mathrm{e}^{\pm\mathrm{i}\mu} \tag{24}$$

$$\Rightarrow \mathrm{i}c_1(+\infty) \cong 2\int_0^\infty \mathrm{d}z\, W\cos\mu \tag{25}$$

and

$$\frac{\mathrm{i}\mathrm{d}c_1(-z)}{\mathrm{d}z} \approx W\mathrm{e}^{\pm\mathrm{i}\gamma} \tag{26}$$

$$\Rightarrow \mathrm{i}c_1(-\infty) \cong 2\int_0^\infty \mathrm{d}z\, W\cos\gamma. \tag{27}$$

This implies that the net inelastic transition probability is

$$P_{01} = \left|2\int_0^\infty \mathrm{d}z\, W\cos\mu\right|^2 - \left|2\int_0^\infty \mathrm{d}z\, W\cos\gamma\right|^2. \tag{28}$$

Using Fourier transforms and the Faltung theorem (Crothers and Holt 1966), it follows that the total cross section is

$$Q_{01}/a_0^2 = 2\pi\int_0^\infty \rho\,\mathrm{d}\rho\, P_{01}(\rho) \tag{29}$$

$$Q_{01}/a_0^2 = \frac{1}{(2\pi v)^2}\int_{|k_0-k_1|}^{k_0+k_1} q\,\mathrm{d}q\int_0^{2\pi}\mathrm{d}\phi\left|\int \mathrm{d}\underline{r}\,\mathrm{e}^{\mathrm{i}\underline{q}\cdot\underline{r}}V_{01}(r)\right|^2 \geqslant 0 \tag{30}$$

where the change in relative momentum of the atomic particles is

$$\underline{q} = \underline{k}_0 - \underline{k}_1 \tag{31}$$

so that

$$q^2 = k_0^2 + k_1^2 - 2k_0k_1\cos\theta \tag{32}$$

where

$$\cos\theta = \hat{\underline{k}}_0\cdot\hat{\underline{k}}_1. \tag{33}$$

Despite inequality (30), $P_{01}(\rho)$ of (28) could, in principle, lie outside the physical range [0, 1] (Bates 1962), in which case, strictly speaking, the perturbation treatment is invalid for the particular ρ-domain. To rephrase, the step leading to (24) becomes invalid. Nevertheless, since $k_0+k_1 > |k_0-k_1|$, the second integral in (28) has the higher frequency leading to greater cancellation. This is illustrated as follows: for $V_{01}(r) \equiv \exp(-\alpha r)$, P_{01} of (28) is given by

$$P_{01} = \frac{4\alpha^2\rho^2}{v^2}[K_1^2(\rho\sqrt{\alpha^2+(k_0-k_1)^2} - K_1^2(\rho\sqrt{\alpha^2+(k_0+k_1)^2}]. \tag{34}$$

However, we have

$$K_1(\zeta) \stackrel{\zeta\gg 1}{\simeq} \sqrt{\frac{\pi}{2\zeta}}\exp(-\zeta) \tag{35}$$

and

$$K_1(\zeta) \stackrel{\zeta\sim 0}{\simeq} \frac{1}{\zeta}. \tag{36}$$

Thus, if we take, say, $\alpha = 1, k_0 = 2$ and $k_1 = 1$ (in atomic units) which are light-particle parameters, we see that the causal term is very much larger than the acausal term, so that the double-perturbation treatment is justified and is consistent; moreover, the link with the first-Born wave treatment (30) is justified.

4. Discussion and conclusions

The quantity Q_{01} (equation (30)) is the quantal first-Born cross section in which the lower limit corresponds to $\theta = 0$ and is causal, whereas the upper limit corresponds to $\theta = \pi$ and is acausal. The classical purely impact parameter first Born approximation comprises $k_0 - k_1 \to (\epsilon_1 - \epsilon_0)/v$ and $k_0 + k_1 \to +\infty$. We may interpret equations (20) and (21) as generalized impact-parameter equations with the first terms on the RHS causal and the second terms acausal, at least as viewed from the derived time-dependent treatment which arises when the acausal terms are neglected. Thus not only does semiclassical mechanics here interpolate between quantal and classical mechanics, but explicitly demonstrates cybernetic effects by which the propagation of waves $-\infty$ to $+\infty$ in time simultaneously invokes propagation of waves $+\infty$ to $-\infty$ in time in a consistently dovetailed unitary manner, the essence of quantum mechanics (here we are not referring to perturbation theory). Clearly our technique, based on the Green function method of (I), generalizes to $U_{00} \neq 0$ and $U_{11} \neq 0$. Moreover, although the semiclassical treatment of Stueckelberg (1932), considered in paragraph 3 of chapter XIII of Mott and Massey (1965), concerns ion–atom collisions, our treatment given above need not be so limited. Our treatment clearly generalizes to any number of coupled states (Bates and Holt 1966). A simple consideration of the leading terms in both versions (with and without the cybernetic, acausal terms) of the first Born approximation shows that the impact-parameter treatment erroneously produces a finite cross section at threshold (Crothers and Holt 1966), whereas the wave treatment (in the form of generalized impact-parameter equations (sic)) at least gives a zero cross section (Wigner 1948).

As presented in this paper, the semiclassical treatment of the four exact first-order equations (8) leads to generalized projectile–target time-dependent interaction impact parameter equations (20), (21). These equations contain acausal behaviour embedded entirely in the $c_j(-z)$ terms, which are absent in the standard impact parameter treatment (see, for example, equation (2.13) of Bichoutskaia *et al* (2002)). The relevance of the approach described, to ultracold collisions, lies in the consideration of equations (20) and (21) in the closely coupled perturbed symmetric resonance model (Crothers 1973) in which both k_0 and k_1 are sufficiently small, that neither causal nor acausal terms can be ignored, relative to each other, $\epsilon_1 - \epsilon_0$ is small and $k_0 - k_1 \neq (\epsilon_1 - \epsilon_0)/v$. The consequence is that a typical very low energy fine-structure ion–atom collision (Devdariani *et al* 2002) will yield to a generalized impact-parameter treatment description of its experimental realization.

In conclusion, in the standard impact-parameter treatment, we may have a straight-line trajectory at impact parameter ρ or indeed, a curved trajectory (e.g. Coulomb), each of which has a point of closest approach, dividing the trajectory into two. On the inward half, this corresponds to radially incoming waves: on the outward half, to radially outgoing waves.

In standard one-dimensional scattering, there are ingoing waves (incident beam) and outgoing waves (transmitted and reflected beams); there are no ingoing waves in the negative direction by assumption.

However, in a three-dimensional spherical interior, *a priori* they may simultaneously be both radially ingoing and outgoing waves in all directions. A counter example is given by the well known plane wave asymptotic expansion

$$\mathrm{e}^{\mathrm{i}\underline{k}\cdot\underline{r}} \overset{kr\gg 1}{\simeq} \frac{2\pi}{\mathrm{i}kr}[\mathrm{e}^{\mathrm{i}kr}\delta(\hat{\underline{k}}-\hat{\underline{r}}) - \mathrm{e}^{-\mathrm{i}kr}\delta(\hat{\underline{k}}+\hat{\underline{r}})] \tag{37}$$

with ingoing waves $\mathrm{e}^{-\mathrm{i}kr}$ (direction $\hat{\underline{r}} = -\hat{\underline{k}}$, momentum $\sim -\hbar k\hat{\underline{r}}$) and outgoing waves $\mathrm{e}^{\mathrm{i}kr}$ (direction $\hat{\underline{r}} = \hat{\underline{k}}$, momentum $\sim +\hbar k\hat{\underline{r}}$). Here, the delta functions are two-dimensional and admittedly there is a problem at $\hat{\underline{k}}\cdot\hat{\underline{r}} = 0$ (Crothers and Mulligan 2002). The picture here is of a wave lying in a plane which sweeps through the spherical interior in the $\underline{k}$ direction, in, say, the $\phi = 0$ plane, ϕ being the cylindrical polar azimuthal angle. The complication, compared to one-dimensional scattering, is that the coordinate $r \in [0, +\infty]$, because the distance between two objects must always be non-negative. The plane wave can represent, in principle, an electron, a photon, an ion, etc impinging on some fixed centre which does not perturb the projectile.

Nevertheless, as semiclassical analysis shows, this comprises a rather classical picture in which the impact parameter is given by $(l + 1/2)/k$ where l is the azimuthal quantum number of the partial wave (see also equation (13)).

When an interaction occurs, however, equations (20)–(23) show that, in quantum mechanics, there are ingoing waves, simultaneously in both halves of the spherical interior, and outgoing waves also in both halves of the interior, in this case $\phi = 0$ and $z \in [-\infty, +\infty]$. From the stationary Schrödinger equation point of view, this is all prescribed instantaneously. From the generalized impact parameter treatment point of view, this comprises acausal cybernetic effects. Of course, this would appear to be implausible at impact energies which are in any way appreciable, but then the generalized treatment does yield the impact-parameter treatment in such a limit.

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