Inversion-symmetry-changing atom-atom collisions*

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Slow collisions of different isotopes of the same species are considered. The adiabatic representation of wave functions is used. There is no restriction to inversion-symmetry-conserving collisions because of the isotopic difference. Such parity-changing collisions are considered and, since levels of different parity can cross, it is shown that the cross sections may be large. The "switching functions," previously used, are shown to play an important role in this reaction and their interpretation is discussed.

In a recent paper[1] it was shown that a careful treatment of m/μ (m is the electron mass, and μ the reduced mass of the atoms) effects leads to corrections to the scattering potentials of order m/μ. It was also shown that the coupling operator between different adiabatic channels is modified in lowest order (μ^{-1}). This arises because the coupling operator comes from the nuclear kinetic energy, which is formally of order μ^{-1}, whereas the electron kinetic energy is of order m^{-1}. Therefore m/μ corrections to T_{e1} can enter the coupling terms in lowest order.

The example of scattering by different isotopes of the same atom was treated, and the equations describing the coupling between two different adiabatic states was obtained. If we drop m/μ corrections wherever possible, these equations are

$$\begin{aligned}(E-T-W_0)F_0-\vec{\mathrm{B}}_{01}\cdot\vec{\nabla}F_1=0\,,\\(E-T-W_1)F_1-\vec{\mathrm{B}}_{10}\cdot\vec{\nabla}F_0=0\,,\end{aligned}\tag{1}$$

where E is the total energy, T is the kinetic energy operator of the colliding atoms, $W_i(R)$ are the usual adiabatic interatomic potentials, and the coupling operators between adiabatic states of opposite (g,μ) inversion symmetry are given by

$$\vec{\mathrm{B}}_{ij}=-\frac{\lambda m}{4\mu}W_{ij}(R)\langle i\,|\sum_i \bar{f}_i|j\rangle\vec{\mathrm{R}}\,.\tag{2}$$

Here $W_{ij}=W_i-W_j$ and

$$\lambda=\Delta M/M_T\,,\tag{3}$$

where ΔM is the difference in masses of the two atoms and M_T is their sum.

The functions $\bar{f}_i=\bar{f}(\vec{\mathrm{x}}_i,\vec{\mathrm{R}})$ are "switching functions" which were introduced by Russek and Schneiderman[2] and used by Thorson[3] and co-workers. Here x_i is the coordinate of the ith electron relative to the internuclear midpoint and R is the internuclear coordinate. The switching function is introduced in order to project an electron onto one or the other atom when the atoms are infinitely separated. The essential part of their definition is the boundary condition

$$\begin{aligned}\lim_{R\to\infty}+\bar{f}(\vec{\mathrm{x}},\vec{\mathrm{R}})&=+1;\quad|\vec{\mathrm{x}}-\tfrac{1}{2}\vec{\mathrm{R}}|\ \text{finite}\\&=-1;\quad|\vec{\mathrm{x}}+\tfrac{1}{2}\vec{\mathrm{R}}|\ \text{finite}\,.\end{aligned}\tag{4}$$

The remaining freedom in the function may be used to optimize some property of the scattering problem. The $\bar{f}_i$ are usefully taken to be odd in both $\vec{\mathrm{x}}$ and $\vec{\mathrm{R}}$. The part of $\vec{\mathrm{B}}_{ij}$ given in Eq. (2) therefore couples states of opposite symmetry. Note that in the limit $\lambda=0$ (when the atoms are no longer different) this coupling vanishes as it should. We also note that in the limit $R\to\infty$ within the matrix element in $\vec{\mathrm{B}}_{ij}$ (half of the electrons are on each atom) so that the coupling operator vanishes in this limit.

The coupling operator is small ($\sim\mu^{-1}$) and may frequently be treated in lowest order, in which case the transition matrix from state 1 to state 0 is

$$T_{10}=-(\mu/2\pi)\langle\psi_1^{(-)}\vec{\mathrm{B}}_{10}\cdot\vec{\nabla}\,\psi_0^{(+)}\rangle\,,\tag{5}$$

where ψ_i satisfies

$$(E-T-W_i)\psi_i^{(\pm)}=0\,,\tag{6}$$

with a unit amplitude plane wave at infinity, and the $(\pm)$ signifies the usual boundary conditions. Chen and Watson[4] have treated a similar matrix element under conditions where an eikonal approximation for the scattering states is possible. These conditions are clearly delineated by them and will not be discussed here.

The eikonal form of $\psi_i^{(\pm)}$ is

$$\psi_i^{(\pm)}=[P_i(\infty)/P_i(R)]^{1/2}e^{\pm iS_i^{(\pm)}(R)}\,,\tag{7}$$

where the local momenta are given by

$$P_i(R)=\{2\mu[E-W_i(R)]\}^{1/2}\,,\tag{8}$$

and the eikonals are given by

$$S_0^{(+)}(R) = \vec{P}_0(\infty)\cdot\vec{R} + \int_{-\infty}^{R} d\vec{s}\cdot[\vec{P}_0(R) - \vec{P}_0(\infty)],$$
$$S_1^{(-)}(R) = \vec{P}_1(\infty)\cdot\vec{R} - \int_{R}^{\infty} d\vec{s}\cdot[\vec{P}_1(R) - \vec{P}_1(\infty)] . \tag{9}$$

By substitution of Eqs. (2), (7), and (9) into the transition matrix with the replacement

$$(\psi_1^{(-)}\vec{B}_{10}\cdot\vec{\nabla}\psi_0^{(+)}) \approx \tfrac{1}{2}i(\psi_1^{(-)}\vec{B}_{10}\cdot[\vec{P}_1(R) + \vec{P}_0(R)]\psi_0^{(+)}),$$

we obtain

$$T_{10} = \frac{i\lambda m}{16\pi}\int d^3R \left(\frac{P_0(\infty)P_1(\infty)}{P_0(R)P_1(R)}\right)^{1/2} \times \vec{R}\cdot[\vec{P}_1(R) + \vec{P}_0(R)]W_{10}(R)\langle 1|\sum_1 \bar{f}_i|0\rangle e^{i\Phi(R)}, \tag{10}$$

where

$$\Phi = -\Delta\vec{P}\cdot\vec{R} + \int_{-\infty}^{R} d\vec{s}\cdot[\vec{P}_0(R) - \vec{P}_0(\infty)] + \int_{R}^{\infty} d\vec{s}\cdot[\vec{P}_1(R) - \vec{P}_1(\infty)] , \tag{11}$$

and

$$\Delta\vec{P} = \vec{P}_1(\infty) - \vec{P}_0(\infty) .$$

The line integrals in (9) and (11) are along the classical paths which are defined as follows. Classical equations of motion are defined by

$$\frac{\partial\vec{P}_i}{\partial\tau} = -\vec{\nabla}W_i(R),$$
$$\frac{\partial\vec{R}}{\partial\tau} = \frac{1}{\mu} - \vec{P}_i. \tag{12}$$

They are integrated for $i = 0$ from the precollision region up to the point $\vec{R}$ with initial conditions specified by $\vec{P}_0(\infty)$ and some impact parameter. The equations for $i = 1$ are integrated backwards in time (τ) from the postcollision region back to the point $\vec{R}$ with starting conditions specified by $\vec{P}_1(\infty)$ and whatever impact parameter is necessary for the path to intersect $\vec{R}$.

Watson[5] has shown that the regions which give the principle contributions are around points $\vec{R} = \vec{R}_0$, which are points of stationary phase, where

$$\vec{P}_0(R_0) - \vec{P}_1(R_0) = 0. \tag{13}$$

This requires that the momentum be continuous in both magnitude and direction, which is just the condition for a classical path. We note that

$$W_{10}(R) = (2\mu)^{-1}[P_0^2(R)] - (2\mu)^{-1}[P_1^2(R)] = (2\mu)^{-1}[\vec{P}_0(R) + \vec{P}_1(R)]\cdot[\vec{P}_0(R) - \vec{P}_1(R)] .$$

In the vicinity of R_0 we define a unit vector $\hat{n}$ along the path so that near R_0

$$W_{10} = (2\mu)^{-1}[P_0(R) + P_1(R)]\hat{n}\cdot[\vec{P}_0(R) - \vec{P}_1(R)] , = (2\mu)^{-1}[P_0(R) + P_1(R)]\hat{n}\cdot\vec{\nabla}\Phi . \tag{14}$$

Then integrating by parts, the T matrix becomes

$$T_{10} = \frac{-\lambda m}{32\pi\mu}\sum_l \int d^3R\,(\hat{n}\cdot\vec{\nabla}\Omega)_l e^{i\Phi_l} , \tag{15}$$

where

$$\Omega = \vec{R}\cdot[\vec{P}_0(R) + \vec{P}_1(R)][P_0(R) + P_1(R)] \times \left(\frac{P_0(\infty)P_1(\infty)}{P_0(R)P_1(R)}\right)^{1/2}\langle 1|\sum_i \bar{f}_i|0\rangle . \tag{16}$$

In (15) the sum over l is a sum over the different points R_{0l}, at which the stationary phase condition is satisfied. The exponential in (15) is a rapidly varying function so that $\hat{n}\cdot\vec{\nabla}\Omega|_{R_0}$ may be removed from the integral. If we drop terms of order $(\mu W/p^2)_l$, then

$$\hat{n}\cdot\vec{\nabla}\Omega|_{R_0} \simeq 4[P_0(\infty)P_1(\infty)]^{1/2} \times P(R_0)\hat{n}\hat{n}:\vec{\nabla}(\vec{R}\langle 1|\sum_i \bar{f}_i|0\rangle)_{R_0} . \tag{17}$$

If the states $\langle 1|$ and $|0\rangle$ are Σ states, then the factor $\langle 1|\sum\bar{f}_i|0\rangle$ will be dependant only on the magnitude of R and not on its direction. Then if there is only one point at which the energy levels of the states cross, that is if $W_{10}(R) = 0$ has only the solution R_0, then the factor $\langle 1|\sum_i \bar{f}_i|0\rangle|_{R_0}$ will be independant of the index l in (15).

We may now write (15) as

$$T_{10} = -\frac{\lambda m}{8\pi\mu}\sum_l [P_0(\infty)P_1(\infty)]^{1/2} \times P[\hat{n}\hat{n}:\vec{\nabla}(\vec{R}\langle 1|\sum_i \bar{f}_i|0\rangle)]_l \int d^3R\, e^{i\Phi_l} , \tag{18}$$

where $P \equiv P_0(R_{0l}) = P_1(R_{0l})$.

Chen and Watson[4] have dealt with this type of integral by expanding Φ_l around the point R_{0l}. They show that it can be reduced to a one-dimensional integral along the classical path passing through R_{0l},

$$\int d^3R\, e^{i\Phi_l} = A_l \int ds\, e^{i\phi_l(s)}, \tag{19}$$

where A_l depends upon the principal radii of curvature of the surfaces of constant eikonal at the point R_{0l} and $\phi_l(s)$ is defined by (11) and evaluated on the path passing through R_{0l} with s measuring the distance away from R_{0l} along this path.

A further expansion of ϕ_l in s can now be per-

formed with the result

$$\phi_l(s) = \Phi(R_{0l}) - \frac{\mu}{2p}(\beta_0 - \beta_1)_l \left(\frac{\partial R}{\partial s}\right)_l s^2 + \cdots, \quad (20)$$

where the β_l are defined by the expansion

$$W_l(R) = W(R_{0l}) + \beta_{ll}(R - R_0) + \cdots,$$

which results in a linear crossing of the states

$$W_0(R) - W_1(R) = (\beta_0 - \beta_1)_l (R - R_0) + \cdots = \beta_{01l}(R - R_0) + \cdots . \quad (21)$$

We emphasize that this real crossing is possible since the states are assumed to have different parity. The resulting integral is

$$\int ds\, e^{i\Phi_l(s)} = e^{i\Phi(R_{0l})}\left[2\pi P/|\beta_{01}(\partial R/\partial s)|_l\right]^{1/2} \times \begin{cases} e^{-i\pi/4} & \text{if } \left(\beta_{01}\frac{\partial R}{\partial s}\right)_l > 0 \\ e^{i\pi/4} & \text{if } \left(\beta_{01}\frac{\partial R}{\partial s}\right)_l < 0 . \end{cases} \quad (22)$$

Substitution back into (18) yields

$$T_{10} = \frac{-\lambda m}{8\pi\mu}\left[P_0(\infty)P_1(\infty)\right]^{1/2}\left(\frac{P}{\mu}\right)^{3/2} \times \sum_l \left[\hat{n}\,\hat{n}:\vec{\nabla}\left(\vec{R}\langle 1|\sum_i \bar{f}_i|0\rangle\right) e^{i\Phi(R_0)} A_l\right] \times \left\{\left[2\pi/|\beta_{10}(\partial R/\partial s)|\right]^{1/2} e^{\pm i\pi/4}\right\}_l . \quad (23)$$

If we assume that there is only one R_0 (only a single crossing of levels), l will take on two values and β_{01} will be independent of l. The factor $(\partial R/\partial s)_l$ will, however, change signs for the two different values of l, since it will be negative on the inward going portion of the curve and positive on the outward. The sign in the factor $(e^{\pm i\pi/4})_l$ will therefore change as l changes, so that this factor will contribute a relative phase of $\pm\frac{1}{2}\pi$ (depending on the sign of β_{01}) between the terms. There will be an additional phase due to the factor $e^{i\Phi(R_{0l})}$.

Further evaluation of (23) requires a solution of the classical-path equations to determine $\hat{n}_l$, $\Phi(R_{0l})$, and A_l at each of the crossings. We may, however, contrast this result with the Landau-Zener result without further calculation. The primary difference (other than the details of the matrix elements) is that curves can cross here and not in the Landau-Zener case. This noncrossing results in a factor $e^{-c/v}$ in the Landau-Zener case, where v is the relative velocity of the nuclei at the crossing point. This velocity is frequently small, so that the energy dependence of the T matrix is dominated by this factor. Equation (22) has no such factor, since levels of opposite parity can cross. Therefore, the cross section may be much larger than that in the Landau-Zener case. The factor $\lambda = \Delta M/MT$ will usually be small, but it is energy independent.

The straight-line impact-parameter treatment of Eqs. (1) is much less general but much simpler than the treatment presented above. The equations are[6]

$$\left(iV\frac{\partial}{\partial z} - W_0\right)A_0 = i\vec{K}\cdot\vec{B}_{01}A_1, \qquad \left(iV\frac{\partial}{\partial z} - W_1\right)A_1 = i\vec{K}\cdot\vec{B}_{10}A_0, \quad (24)$$

where the A_i are the amplitudes of the two states which are functions of the impact parameter b and where V is the relative velocity of the collision and $\vec{K} = m\vec{V}$. Again assuming B_{10} is small, we obtain

$$A_1(b) = \frac{1}{V}\int_{\infty}^{\infty} dz\,\vec{K}\cdot\vec{B}_{10}\exp\left(-i/V\int_{-\infty}^{z} dz'\,W_{01}\right), \quad (25)$$

which with the aid of (2) and an integration by parts can be written as

$$A_1 = \frac{\lambda m V}{z}\int_0^{\infty} dz\,\frac{d}{dz}\left(z\langle 0|\sum_i \bar{f}_i|1\rangle\right) \times\cos\left(\frac{1}{V}\int_0^z dz'\,W_{01}\right). \quad (26)$$

We have used the fact that $\langle 0|\sum_i \bar{f}_i|1\rangle$ is an even function of z. In the limit of low collision velocity the last factor in (26) oscillates rapidly, so that the principle contribution comes from the point of stationary phase. The result is then

$$A_1(b) = \frac{\lambda m V}{2}\left(\frac{\pi V(R_0^2 - b^2)^{1/2}}{|\beta_{01}|R_0}\right)^{1/2} \times\frac{d}{dR}\left((R^2 - b^2)^{1/2}\langle 0|\sum_i \bar{f}_i|1\rangle\right), \quad R_0 > b = 0, \quad R_0 < b . \quad (27)$$

Note that for small V the cross section given by

$$\sigma = \int d^2 b\,|A_1(b)|^2 \quad (28)$$

is proportional to $E^{3/2}$ rather than the more rapid dependence in the avoided crossing case.

The remaining novel feature of this result is the over-all factor $\langle 1|\sum_i \bar{f}_i|0\rangle|_{R_0}$ in the T matrix. The cross section for this process therefore provides a direct measurement of an integral containing the switching function. The function is arbitrary except for its boundary condition [Eq. (4)]. This may be viewed in two ways: It can either be thought of

as a flaw in the theory in that the cross section is arbitrary to the extent that the switching function is arbitrary, or the function can be thought of as an additional freedom in a trial wave function. This additional freedom may be exploited to optimized some scattering property. This latter was the attitude taken in Ref. 1. In either case, the switching function seems to be a necessary ingredient in arriving at equations such as (1); that is, I know of no technique for a many-electron problem which exploits the adiabatic representation, treats the Pauli principle correctly, treats the boundary conditions correctly, and arrives at coupled channel equations which does not introduce something akin to the switching functions.

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