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Résumé.– Nous présentons une formulation de la théorie moléculaire des collisions atomiques qui satisfait les conditions aux limites de diffusion, et ce sans avoir recours à la notion de facteur de translation électronique.

Abstract.– We present a formulation of the molecular theory of atomic collisions satisfying correct scattering boundary conditions, without resorting to the notion of electron translation factor.

1. Introduction

The molecular model of slow ion-atom and atom-atom collisions, or the perturbed-stationary-state method [1], has been widely used in studying inelastic processes like charge exchange and impact excitations [2-6]. The basic idea is to expand the scattering wave function in adiabatic Born-Oppenheimer (BO) electronic states. These states are usually assumed to couple non-adiabatically by the relative motion of the nuclei, i.e. through the action of the corresponding kinetic-energy operator. The molecular model is known to suffer from two fundamental difficulties [7,8]. The first problem is that proper scattering boundary conditions are not satisfied, as the non-adiabatic (NA) matrix elements are not necessarily vanishing asymptotically. Secondly, the NA matrix elements are not translationally invariant. That is, they depend on the molecular origin chosen for the coordinate system of electrons. The common approach [9] to remove these difficulties has been to modify the BO electronic functions by an electron-translation factor (ETF). The ETF is a nuclear-velocity phase-like term that takes account of the fact that in the asymptotic limit the electron actually "travels" with "its" nucleus. The couplings between the ETF modified functions vanish asymptotically, so that scattering boundary conditions are fulfilled. However, the couplings change also in the molecular region thereby affecting the scattering cross section. Aside from the requirement for proper asymptotic behaviour the form of the ETF is arbitrary [5]. Several ETF optimization methods [2-6] are currently in use, but we shall not review them. Our purpose here is to show that a molecular model of atomic collisions which satisfies scattering boundary conditions can be formulated without the ETF. For simplicity we shall consider a diatomic molecule made of one electron and uneven nuclei A and B having charge and mass Z_A; m_A and Z_B; m_B, respectively. Atomic units are

employed in all the equations.

2. Adiabatic electronic states.

To describe the relative motions of the electron and the nuclei A and B two internal vectors are required. In a molecular frame they are of the general form [5,10],

$$\vec{R} = \vec{R}_B - \vec{R}_A\,; \qquad \vec{r} = \vec{r}_e - p\vec{R}_A - q\vec{R}_B\,; \qquad p+q=1, \tag{1}$$

where $\vec{r}_e$, $\vec{R}_A$ and $\vec{R}_B$ are the instantaneous positions of the electron and the nuclei in the laboratory frame. In these coordinates the BO Hamiltonian reads

$$H_{BO} = -\frac{1}{2}\Delta_r - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} + \frac{Z_A Z_B}{R}\,, \tag{2}$$

where Δ_r is the Laplacian in $\vec{r}$ and

$$\vec{r}_A = \vec{r} - q\vec{R}\,; \qquad \vec{r}_B = \vec{r} + p\vec{R}\,. \tag{3}$$

The Hamiltonian (2) describes the motion of a rest-mass electron in the cylindrical electrostatic field of the nuclei A and B separated by a fixed distance R. The adiabatic electronic states are the eigenfunctions of H_{BO} satisfying

$$H_{BO}(\vec{R},\vec{r})\,\psi_\alpha = U_\alpha(R)\,\psi_\alpha(\vec{R},\vec{r})\,, \tag{4}$$

where α denotes all the one-electron quantum numbers. The BO energy U_α depends implicitly on R which determines the cylindrical electrostatic field. The adiabatic functions $\{\psi_\alpha\}$ depend also on the relative orientation of the nuclei [10,11] through $\vec{r}$. It is convenient to describe $\vec{r}$ in a body-fixed frame whose z-axis coincides with $\vec{R}$. This way the electronic functions have cylindrical symmetry and belong to the irreducible representations of the point group $C_{\infty v}$ [4,10,11].

The adiabatic electronic basis $\{\psi_\alpha\}$ is complete at every R. Let us now examine its behaviour in the large R limit. Since R is constant in the BO approximation, then $\Delta_r = \Delta_{r_A} = \Delta_{r_B}$, and H_{BO} can be broken in two ways

$$H_{BO} = H_A + V_B = H_B + V_A\,, \tag{5}$$

where

$$H_A == -\frac{1}{2}\Delta_{r_A} - \frac{Z_A}{r_A}\,; \qquad V_B = -\frac{Z_B}{|\vec{r}_B + \vec{R}|} + \frac{Z_A Z_B}{R}\,, \tag{6a}$$

$$H_B == -\frac{1}{2}\Delta_{r_B} - \frac{Z_B}{r_B}\,; \qquad V_A = -\frac{Z_A}{|\vec{r}_A - \vec{R}|} + \frac{Z_A Z_B}{R}\,. \tag{6b}$$

Here H_A (H_B) is the Hamiltonian of one rest-mass electron moving in the central field of nucleus A (B), and V_B (V_A) is the electrostatic perturbation of nucleus B (A) situated at a distance R from the center. It is clear that in the limit $R \to \infty$ H_{BO} goes either to H_A or to H_B. The asymptotic adiabatic basis and spectrum $\{\psi_\alpha\}$; $\{U_\alpha\}$ are, respectively, the union of the atomic bases and spectra $\{\Phi_a\}$; $\{U_a\}$ and $\{\Phi_b\}$; $\{U_b\}$ satisfying

$$H_A(\vec{r}_A)\Phi_a(\vec{r}_A) = U_a\Phi_a(\vec{r}_A)\,, \tag{7a}$$

$$H_B(\vec{r}_B)\Phi_b(\vec{r}_B) = U_b\Phi_b(\vec{r}_B)\,. \tag{7b}$$

The adiabatic electronic basis is therefore partitioned into two channel subsets $\{\psi_\alpha\}$ and $\{\psi_\beta\}$ according to the limiting behaviour of the BO functions and energies,

$$\lim_{R\to\infty}\psi_\alpha \to \Phi_a\,; \qquad \lim_{R\to\infty} U_\alpha \to U_a\,, \tag{8a}$$

$$\lim_{R\to\infty}\psi_\beta \to \Phi_b\,; \qquad \lim_{R\to\infty} U_\beta \to U_b\,. \tag{8b}$$

In other words, neglecting electron mass-polarization (EMP) effects (see below) the adiabatic electronic functions are the correct asymptotic states of the electron. For this reason alone it does not make sense to modify these functions by an ETF. It is shown below how to impose correctly scattering boundary conditions in the molecular model.

3. Scattering equations in the molecular frame.

Consider the charge exchange system

$$A + B^+ \longleftrightarrow A^+ + B\,. \tag{9}$$

In order to write the scattering equations it is convenient to separate first the center-of-mass (COM) motion of the two nuclei and the electron. To that end a set of internal-motion coordinates must be decided on. The molecular-frame vectors $(\vec{R},\vec{r})$ defined in (1) are inappropriate for scattering as the limit $R \to \infty$ implies $r \to \infty$ as well. That is, in the asymptotic limit the molecular model forbids free atomic species and prevents thereby imposing scattering boundary conditions [11]. A correct internal frame for collisions must have the distance between the COM of the atomic species as the scattering coordinate. Usually there are several such coordinates as the limiting atomic species depend on the asymptotic channel. Let us designate the channels in our simple system by the atom, i.e. where the electron resides. The left-hand side of (9) is therefore channel A wheres channel B is on the right. The corresponding internal coordinates are $(\vec{\rho}_A,\vec{r}_A)$ and $(\vec{\rho}_B,\vec{r}_B)$, where $\vec{\rho}_A$ and $\vec{\rho}_B$ are the nucleus-atom distance vectors given by

$$\vec{\rho}_A = \vec{R}_B - (m_A+1)^{-1}(m_A\vec{R}_A + \vec{r}_e) \tag{10a}$$

$$\vec{\rho}_B = (m_B+1)^{-1}(m_B\vec{R}_B + \vec{r}_e) - \vec{R}_A \tag{10b}$$

Separating the COM of motion the internal Hamiltonian of the system can be expressed in the two channel coordinate frames as follows

$$H^A = T_A + T_{EA} + H_A(\vec{r}_A) + V_B(\vec{R},\vec{r}_A)\,, \tag{11a}$$

$$H^B = T_B + T_{EB} + H_B(\vec{r}_B) + V_A(\vec{R},\vec{r}_B)\,. \tag{11b}$$

where H_A, (H_B) and V_B (V_A) are defined in (6); T_{EA} (T_{EB}) is the EMP in atom A (B),

$$T_{EA} = -\frac{1}{2m_A}\Delta_{r_A}\,, \tag{12a}$$

$$T_{EB} = -\frac{1}{2m_B}\Delta_{r_B}\,; \tag{12b}$$

and T_A (T_B) is the scattering-energy operator in channel A (B)

$$T_A = -\frac{1}{2\mu_A}\Delta_{\rho_A}\,; \qquad \mu_A = \left[\frac{1}{m_A+1}+\frac{1}{m_B}\right]^{-1}, \tag{13a}$$

$$T_B = -\frac{1}{2\mu_B}\Delta_{\rho_B}\,; \qquad \mu_B = \left[\frac{1}{m_A}+\frac{1}{m_B+1}\right]^{-1}. \tag{13b}$$

Inspecting (11) we see that the channel internal Hamiltonians consist of the BO Hamiltonian, either as $H_A + V_B$ or $H_B + V_A$, and two kinetic-energy terms. The atomic EMP operators induce small shifts in the atomic energy levels, a few cm^{-1} at most [12]. The effect on the atomic wave function is by far less, and can hardly influence the scattering cross sections (see below). Neglecting the atomic EMP terms in (11), it is clear that the adiabatic BO electronic basis is a perfect choice to expand the scattering wave function. Of course, one can expand also in the asymptotic atomic states, but this expansion is slower convergent because the atomic states are unperturbed by the molecular field. That is, in the molecular region the coupling between atomic states is due to the electrostatic field of the second nucleus. The BO electronic functions, on the other hand, adjust themselves infinitely fast to the change of field due to the motion of the nuclei. In reality they cannot do so, resulting in dynamical couplings from the action of the scattering-energy operators.

It is evidently computationally advantageous to work in the molecular frame where the electronic functions and their couplings are easily obtained [13]. However, we must express the the scattering-energy operators T_A and T_B in terms of the molecular vectors $\vec{R}$ and $\vec{r}$. This is achieved using the following transformations of the internal vectors

$$\vec{R} = \vec{\rho}_A + (m_A+1)^{-1}\vec{r}_A\,; \qquad \vec{r} = \left[1 - q(m_A+1)^{-1}\right]\vec{r}_A - q\vec{\rho}_A\,, \tag{14a}$$

$$\vec{R} = \vec{\rho}_B - (m_B+1)^{-1}\vec{r}_B\,; \qquad \vec{r} = \left[1 - p(m_B+1)^{-1}\right]\vec{r}_B + p\vec{\rho}_B\,, \tag{14b}$$

and applying the chain rule to the Laplacians in $\vec{\rho}_A$ and $\vec{\rho}_B$. In the molecular frame both scattering-energy operators comprise three terms

$$T_A = T_N + T_{NE} + T_{EM}\,; \qquad T_B = T_N + T_{NE} + T_{EM}\,, \tag{15}$$

where

$$T_N = -\frac{1}{2\mu}\Delta_R\,; \qquad T_{NE} = -\frac{f}{2}\{\nabla_R, \nabla_r\}\,; \qquad T_{EM} = -\frac{g}{2}\Delta_r\,, \tag{16}$$

with { , } signifying anti-commutation relation, and μ, f and g are channel-dependent mass factors

$$\mu = \mu_A\,; \qquad f = -\frac{q}{\mu_A}\,; \qquad g = \frac{q^2}{\mu_A}\,, \tag{17a}$$

$$\mu = \mu_B\,; \qquad f = \frac{p}{\mu_B}\,; \qquad g = \frac{p^2}{\mu_B}\,. \tag{17b}$$

The operator T_N is the kinetic-energy operator for the relative motion of the nuclei along $\vec{R}$. The second term T_{NE} is a nuclear-electronic (NE) momentum coupling operator. The third operator T_{EM} is an EMP term in the molecular frame. It arises because

the reduced mass of the molecular electron differs from the atomic values. The NE term expresses the fact that the electron is actually moving with its nucleus. In other words, T_{NE} assumes the role of the ETF. Combined NA, NE and EMP couplings are translationally invariant for a given channel. They vary between the channels, but this is obvious since the scattering-energy operators are different.

Transforming the atomic EMP terms (12) to the molecular frame using (14) and the chain rule we obtain

$$T_{EA} = -\frac{1}{2}\Big[\frac{1}{m_A(m_A+1)^2}\Delta_R + \frac{(m_A+p)}{m_A(m_A+1)^2}\{\nabla_R,\nabla_r\} + \frac{(m_A+p)^2}{m_A(m_A+1)^2}\Delta_r\Big], \tag{18a}$$

$$T_{EB} = -\frac{1}{2}\Big[\frac{1}{m_B(m_B+1)^2}\Delta_R + \frac{(m_B+q)}{m_B(m_B+1)^2}\{\nabla_R,\nabla_r\} + \frac{(m_B+q)^2}{m_B(m_B+1)^2}\Delta_r\Big]. \tag{18b}$$

Comparing the result above with (15), (16) and (17), it is clear that by including the atomic EMP terms the mass factors in the molecular-frame operators T_N, T_{NE} and T_{EM} have to be redefined. Quantitatively the change is minuscule, on the order of the reciprocal atomic masses at most. It cannot affect inelatstic process in any meaningful way. But the inclusion of atomic EMP in the molecular model prevents exact scattering boundary conditions from being fulfilled. With atomic EMP there will always be asymptotic couplings, reflecting the fact that the real atomic energies are slightly shifted as compared with the adiabatic values satisfying (8). It is therefore necessary to neglect atomic EMP in the molecular model. The error introduced this way is mainly in the scattering energy, and is definitely negligible. Notice that without atomic EMP the internal channel Hamiltonians are slightly different.

Expanding the outgoing scattering wave function in the adiabatic electronic states [4,11]

$$\Psi(\vec{R},\vec{r}) = \sum_{\alpha}\chi_\alpha(\vec{R})\,\psi_\alpha(\vec{R},\vec{r}), \tag{19}$$

the Schrödinger equation for the internal Hamiltonian minus the atomic EMP terms, can be reduced into a set of coupled equations for the scattering amplitudes χ_α

$$\Big[\frac{-1}{2\mu}\Delta_R + U_\alpha(R) - E\Big]\chi_\alpha(\vec{R}) = \sum_{\alpha'}(\vec{A}_{\alpha,\alpha'}\cdot\vec{N} + B_{\alpha,\alpha'})\chi_{\alpha'}(\vec{R}). \tag{20}$$

The amplitudes are coupled by a differential operator $\vec{N}$ whose spherical components are given by [4,10]

$$N^R = \frac{\partial}{\partial R}\,; \qquad N^\theta = \frac{1}{R}\frac{\partial}{\partial\theta}\,; \qquad N^\phi = \frac{1}{R\sin\theta}\frac{\partial}{\partial\phi}\,. \tag{21}$$

The action of $\vec{N}$ as a function of R is scaled by the matrix elements of a first-derivative electronic coupling operator $\vec{A}$,

$$\begin{aligned} A^R &= \mu^{-1}\frac{\partial}{\partial R} + ifK_z\,; \\ A^\theta &= -i\Big[(\mu R)^{-1}L_y - fK_x\Big]\,; \\ A^\phi &= i\Big[(\mu R)^{-1}(L_x - \cot\theta\,L_z) + fK_y\Big], \end{aligned} \tag{22}$$

where $\vec{K}$ and $\vec{L}$ are the linear and the orbital angular momenta of the electron. The scattering amplitudes are also coupled by the matrix elements of a second-derivative electronic operator B given by

$$B = T_N + T_{NE} + T_{EM} . \tag{23}$$

4. Discussion

Equations (16), (17) and (19) to (23) describe the collision of a nucleus and a one-electron atom in the molecular frame. Solving the coupled equations (20) gives the exact scattering amplitudes $\{\chi_\alpha\}$ in terms of the internuclear distance $\vec{R}$. The molecular model provides a unified description of all channels involved in the collision. The distinction between the channels is not via the channel-dependent scattering coordinate, but through the mass factors (17) appearing in the operators (22) and (23) which couple the adiabatic electronic states. As a result the coupling of states from different channels is not hermitian. This is manifested, for example, in charge exchange cross sections (see below).

In the molecular frame the coupling of adiabatic electronic states originates from several sources. Firstly, there is a NA term related to T_N (e.g. $\mu^{-1}\frac{\partial}{\partial R}$ or $-i(\mu R)^{-1}L_y$). This is the dynamical coupling that is usually accounted for in applications. Then there is a NE term originating from T_{NE} (e.g. ifK_z or ifK_x). Lastly, we have an EMP part T_{EM}, but only in the second-derivative electronic operator B. To the knowledge of the author, NE momentum couplings and EMP terms have always being ignored in molecular treatments of atomic collisions. Momentum couplings enter the formulation whenever the particles are described in moving frames. They are the analogue of noninertial forces in a dynamical description which is not within the Hamiltonian framework. In this respect NE and EMP interactions actually play the role that was originally assigned to the ETF [9], i.e. they take account of the fact that the electron actually "travels" with "its" nucleus. To see this notice that each individual NE and EMP matrix element is origin dependent because of the constants f and g [see (17)]. This implies that the NA matrix elements must be origin dependent, since the scattering-energy operator in each channel is Galilean invariant. In other words NE and EMP terms correct for the origin dependence of NA couplings. At the same time they also eliminate residual asymptotic couplings. Suppose that the origin is selected on nucleus A, so that $q = 0$ and the coupling elements appearing in channel-A rows of the coupled equations are precisely the NA terms. From (8) it follows that with this choice the NA couplings of channel A must vanish asymptotically [14]. This is certainly not the case for other origins, say, nucleus B [7-9]. However, as the combined NA, NE and EMP coupling is translationally invariant, it follows that NE and EMP terms render also the correct boundary conditions.

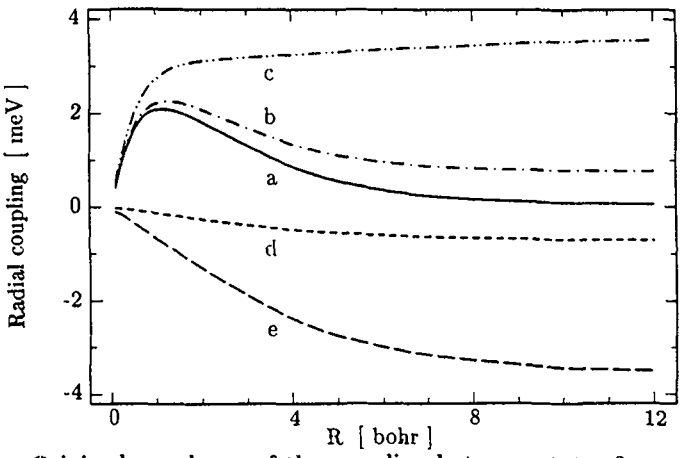

Fig. 1. – Origin dependence of the coupling between states $2p\pi_x$ and $3p\pi_x$.

Figure 1 depicts the dependence on R of matrix elements of the first-derivative radial coupling operators $\mu^{-1}\frac{\partial}{\partial R}$ (NA), ifK_z (NE), and the combined invariant term A^R, between two states of $^4HeH^{++}$ which dissociate to excited states of He^+ (channel A). The invariant coupling in this figure is curve (a) which is the NA matrix element computed with the origin placed on He^{++}. It clearly goes to zero as $R \to \infty$. Curves (b) and (c) are the same NA matrix element for the nuclear-COM and H^+ origins, respectively. These two curves do not vanish asymptotically. Curves (d) and (e) are the corresponding NE matrix elements. It is evident from figure 1 that the combined NA and NE for each origin is curve (a). It should be emphasized that the invariant coupling here is hermitian because the two electronic states dissociate to the same atom. The situation is of course different with couplings of states belonging to distinct channels. Figure 2 shows the first-derivative invariant radial coupling of two states of $^4HeH^{++}$, one dissociating to an excited state of He^+ while the other to the ground state of hydrogen. There is pronounced difference between the coupling in the helium ion [curve (a)] and hydrogen [curve (b)] rows of the coupled equations. The reason is the difference in nuclear charge. Clearly He^{++} binds the electron more strongly than proton does, and is less willing to lose it on impact. Hence, couplings in the He^+ channel are attenuated as compared with those of H (see Fig. 2) The total charge-exchange cross sections in collisions of H^+ and $He^+(n = 1)$ are indeed two to three orders of magnitude smaller than when He^{++} impacts on $H(n = 1)$ [15,16].

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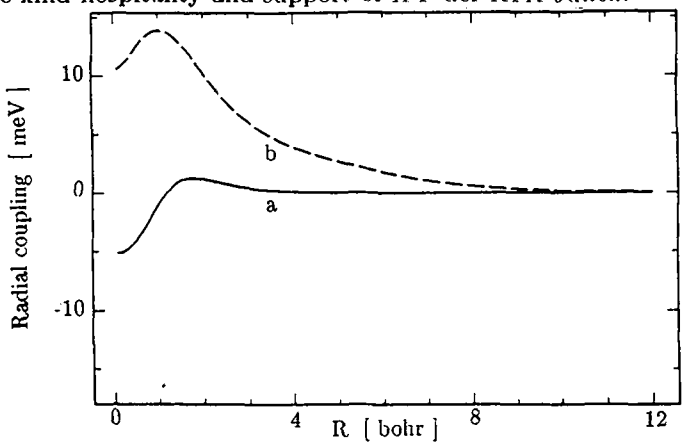

Fig. 2. – The coupling between states $1s\sigma$ and $2p\sigma$.

References

[1] N.F. Mott and H.S.W. Massey, *The Theroy of Atomic Collisions* (Oxford University Press, London, 1952), p. 153.
[2] J.S. Briggs, Rep. Prog. Phys., **39**, 217 (1976).
[3] Dz. Belkic, R. Gayet and A. Salin, Phys. Rep. **56**, 279 (1979).
[4] J.B. Delos, Rev. Mod. Phys. **53**, 287 (1981).
[5] R. McCarroll, in *Atomic and Molecular Collision Theory*, edited by F.A. Gianturco (Plenum, New York, 1982), p. 165.
[6] B.H. Brandsen, *Atomic collision theory* (Benjamin, Reading, 1983).
[7] D.R. Bates, H.S.W. Massey and A.L. Stewart, Proc. Roy. Soc. A **216**, 437 (1953).
[8] A. Riera and A. Salin, J. Phys. B **9**, 2877 (1976).
[9] D.R. Bates and R. McCarroll, Proc. Roy. Soc. A **245**, 175 (1958).
[10] W. Kolos and L. Wolniewicz, Rev. Mod. Phys. **35**, 473 (1963).
[11] B.C. Garett and D.G. Truhlar in *Theoretical Chemistry: Advances and Perspectives*, edited by D. Hendersen (Academic, New York, 1981), Vol. **6A**, p. 215.
[12] H.A. Bethe and E.E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms*, (Springer, Berlin, 1957), p. 169.
[13] A. Macias and A. Riera, Phys. Rep. **90**, 301 (1982).
[14] R.D. Piacentini and A. Salin, J. Phys. B **7**, 1666 (1974).
[15] B. Peart, R. Grey and K.T. Dolder J. Phys. B **10**, 2675 (1977).
[16] W.L. Nutt, R.W. McCullough, K. Brady, M.B. Shah and H.B. Gilbody, J. Phys. B **11**, 1457 (1978).