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Impact-parameter treatment of high-velocity electron capture from diatomic molecules at fixed orientation

Y. D. Wang and J. H. McGuire
J. R. McDonald Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506

R. D. Rivarola
Instituto de Fisica Rosario, Universidad Rosario, 2000 Rosario, Argentina

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Scattering of charged particles at high velocity from diatomic molecules is formulated in the impact-parameter treatment using a Fourier transform of the amplitude in the quantum-mechanical treatment. Probabilities and total cross sections are evaluated for electron capture for a fixed orientation of the intermolecular axis. Total cross sections, integrated over projectile impact parameters, for capture from H_2 predict variations of a factor of 2 or more for various orientations of the molecular axis. Capture from heteronuclear diatomic molecules is also considered.

I. INTRODUCTION

The impact-parameter treatment has been widely used in atomic scattering to evaluate probabilities and cross sections for various reactions including electron capture. In comparison to the more rigorous quantum-mechanical wave treatment where the projectile is treated as a wave packet, in the impact-parameter treatment the projectile is regarded more simply as a localized classical particle. The impact-parameter treatment has the advantage that the correct probability may not be larger than one, and that multiple scattering (e.g., double electron capture) can be evaluated in the independent particle approximation by simple multiplication of probabilities for each scattering. In this paper we formulate impact-parameter treatment for electron capture from simple diatomic molecules by taking a Fourier transform of the quantum-mechanical wave amplitude. We give particular attention to interference terms. Probabilities and total cross sections are evaluated as a function of the orientation of the axis of the molecule for electron capture from diatomic molecules at high collision velocities in the impact-parameter representation.

Evaluation of total cross sections in the quantum-mechanical wave treatment for electron capture from H_2 by high-velocity protons was first done by Tuan and Gerjuoy[1] in 1960, and later considered by Band[2] and by Ray and Saha.[3,4] While it was recognized that the outgoing waves produced interference patterns typical of scattering from two centers, these authors averaged over the orientation of the molecule, thus averaging out the interference pattern. Recently Deb, Jain, and McGuire[5] have reported calculations of differential cross sections at forward scattering angles for fixed orientation of the molecular axis which show explicitly the interference pattern from the two atomic centers. All of the previous theoretical work was done in the quantum-mechanical wave treatment. In this paper we consider the impact-parameter treatment of electron capture from molecules. No experiments are presently available for these differential cross sections, but using Coulomb explosion techniques to determine the orientations of the intermolecular axis, it is now possible[6] to observe total cross sections for electron capture at fixed intermolecular orientation. Here we present calculations for these observable total cross sections as well as the impact-parameter dependences of these cross sections. We find variations greater than a factor of 2 in the cross sections as a function of the internuclear orientation.

In Sec. II we formulate scattering from diatomic molecules in the impact-parameter treatment. In Sec. III we first use some simple linear combination of atomic orbital (LCAO) wave functions and develop general expressions. Then we apply these expressions and Weinbaum wave function[7] to calculate probabilities and cross sections for electron capture at high velocities from H_2 at fixed orientation within the Brinkman-Kramers (BK) approximation.[8] Generalization of our results to heteronuclear systems is done in Sec. III C. In Sec. IV we discuss various aspects of our results. Atomic unit is used throughout unless otherwise stated.

II. FORMULATION

Here we obtain the probability amplitude for particle scattering at a fixed impact parameter **B** from a diatomic molecule by Fourier transforming the T matrix for quantum-mechanical wave scattering.

To establish an expression for molecular T matrix (hereafter denoted as T_M) of scattering from a diatomic molecule, we will treat the diatomic molecule as a system containing two effective atomic scatterers centered on each nuclei. Using the well-known expansion[9,10] to treat multicenter scattering and ignoring rescattering between the effective centers, one can express T_M as

$$\begin{aligned} T_M &= (T_1+T_2)+(T_1G_0T_2+T_2G_0T_1)+\cdots \\ &\cong T_1+T_2 , \end{aligned} \tag{1}$$

where T_j ($j=1,2$) stands for the individual T matrix for each effective center. An effective atomic center in a molecule is not quite the same as an isolated free atom. It will be shown that the T matrix for an isolated atom and an atomic center in a molecule differ by an overall constant. For high-velocity collisions we ignore vibration and rotation of the molecule, which is effectively frozen during the relatively quick collision.

For scattering from two centers illustrated in Fig. 1, it is convenient to place the origin of all coordinates at the center of mass of the system. Then the atomic centers are displaced from the center of mass by $(1-\mu)\boldsymbol{\rho}$ and $-\mu\boldsymbol{\rho}$ for center 1 and center 2, respectively, where $\mu=M_1/(M_1+M_2)$. It is well known that displacing the origin of the coordinates by a distance $\mathbf{d}$ corresponds to[9,10]

$$T_j(\mathbf{d})=e^{-i\boldsymbol{\alpha}\cdot\mathbf{d}}T_j(0)\ , \tag{2}$$

with $\boldsymbol{\alpha}=\mathbf{K}_f-\mathbf{K}_i$. Consequently, we have

$$\begin{aligned}T_M\cong T_1+T_2&=T_1(0)e^{-i(1-\mu)\boldsymbol{\alpha}\cdot\boldsymbol{\rho}}+T_2(0)e^{i\mu\boldsymbol{\alpha}\cdot\boldsymbol{\rho}}\\&=t_1e^{-i(1-\mu)\boldsymbol{\alpha}\cdot\boldsymbol{\rho}}+t_2e^{i\mu\boldsymbol{\alpha}\cdot\boldsymbol{\rho}}\end{aligned} \tag{3}$$

with respect to the center of mass of the molecule. Here $T_j(0)=t_j$ is the atomic T matrix for center j where the projectile interacts with the effective atomic center with no displacement. Thus the relative phase between T_1 and T_2 due to the internuclear displacement $\boldsymbol{\rho}$ is $\boldsymbol{\alpha}\cdot\boldsymbol{\rho}$, independent of the choice of origin of the coordinate system. As a consequence the quantum waves scattering from the diatomic molecule produce an interference pattern characteristic of scattering from two centers.[5]

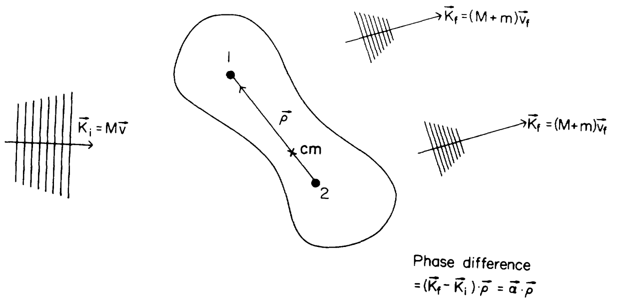

FIG. 1. Illustration of quantum-mechanical wave treatment for a diatomic molecule. On the left is the incident plane wave with wave vector $\mathbf{K}_i$; on the right are the scattered waves from center 1 and center 2 with wave vector $\mathbf{K}_f$.

Now we find the corresponding probability amplitude for scattering by a particle with a straight-line trajectory $\mathbf{R}=\mathbf{B}+\mathbf{v}t$ passing through the center of mass of the molecule at $t=0$ and $\mathbf{B}=0$. The probability amplitude $a\,(\mathbf{B})$ is, in general, related to the T matrix by a Fourier transformation,[11,12] namely,

$$a(\mathbf{B})=\frac{1}{v}\int e^{i\boldsymbol{\alpha}_\perp\cdot\mathbf{B}}T\,d^2\alpha_\perp\ , \tag{4}$$

where $\boldsymbol{\alpha}_\perp$ is perpendicular to the projectile velocity $\mathbf{v}$ taken to define the z axis of the system. Thus taking and using Eq. (3) and Eq. (4) we have a general expression for the probability amplitude, namely,

$$\begin{aligned}a_M(\mathbf{B})&=\frac{1}{v}\int e^{i\boldsymbol{\alpha}_\perp\cdot\mathbf{B}}(t_1e^{-i(1-\mu)(\boldsymbol{\alpha}_\perp\cdot\boldsymbol{\rho}_\perp+\alpha_z\rho_z)}+t_2e^{i\mu(\boldsymbol{\alpha}_\perp\cdot\boldsymbol{\rho}_\perp+\alpha_z\rho_z)})d^2\alpha_\perp\\&=\frac{e^{-i(1-\mu)\alpha_z\rho_z}}{v}\int e^{i\boldsymbol{\alpha}_\perp\cdot[\mathbf{B}-(1-\mu)\boldsymbol{\rho}_\perp]}t_1d^2\alpha_\perp+\frac{e^{i\mu\alpha_z\rho_z}}{v}\int e^{i\boldsymbol{\alpha}_\perp\cdot(\mathbf{B}+\mu\boldsymbol{\rho}_\perp)}t_2d^2\alpha_\perp\\&=e^{-i(1-\mu)\alpha_z\rho_z}a_1[\mathbf{B}-(1-\mu)\boldsymbol{\rho}_\perp]+e^{i\mu\alpha_z\rho_z}a_2(\mathbf{B}+\mu\boldsymbol{\rho}_\perp)\\&=(a_1+a_2e^{i\delta})e^{-i(1-\mu)\alpha_z\rho_z}\equiv a_1'+a_2'e^{i\delta}\ ,\end{aligned} \tag{5}$$

where $\delta=\alpha_z\rho_z$, and $e^{-i(1-\mu)\alpha_z\rho_z}$ is an overall phase dependent on the choice of origin of the coordinate system. This overall phase may be ignored in the evaluation of physical observables such as $|a_M|^2$. Then the net probability for scattering from a diatomic molecule is given by

$$P_M=|a_M|^2=|a_1|^2+|a_2|^2+2\,\mathrm{Re}(a_1a_2e^{i\delta})\ . \tag{6}$$

This is of the form of a vector sum, i.e., $\mathbf{a}_M=\mathbf{a}_1+\mathbf{a}_2$ where $P_M=|a_M|^2$. Note that $\mathbf{B}-(1-\mu)\boldsymbol{\rho}_\perp=0$ and $\mathbf{B}+\mu\boldsymbol{\rho}_\perp=0$ correspond to trajectories passing through centers 1 and 2, respectively. Also the phase difference δ is independent of the choice of origin of the coordinates, i.e., independent of μ.

In the impact parameter treatment illustrated in Fig. 2, the probability amplitude a_M is the sum of an amplitude a_1 from center 1 at position $(1-\mu)\boldsymbol{\rho}$ relative to the

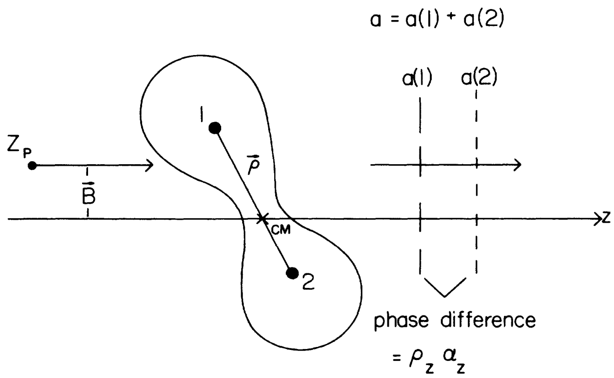

FIG. 2. Illustration of impact-parameter picture for a diatomic molecule. $\boldsymbol{\rho}$ is the molecular axis vector that defines orientation of the molecule. CM denotes center of mass of atom 1 and atom 2. Z_p is the charge of the projectile, $\mathbf{B}$ is the impact parameter. $a(1)$ and $a(2)$ are amplitudes from center 1 and center 2, and a is the total probability amplitude.

center of mass, plus an amplitude a_2 from center 2 at $-\mu\boldsymbol{\rho}$. The amplitudes a_1 and a_2 have a phase difference $\delta=\alpha_z\rho_z$ arising from the separation of the two centers. For heavy projectiles, i.e., $M_p \gg 1$, such as we consider in this paper, one has to order $(1/M_p)$, $\alpha_{\min}=K_f-K_i$, the minimum momentum transfer. For electron capture, using overall energy conservation,[13] one can obtain $\alpha_{\min}=K_f-K_i \cong v/2-\Delta E/v \cong \alpha_z$, where $\Delta E=E_f-E_i$.

III. CALCULATIONS

In this section we evaluate $1s$-$1s$ cross sections for electron capture from diatomic molecules at high collision velocities. First we consider homonuclear molecules, in particular, H_2. Then we consider heteronuclear molecules. In this section we shall apply the simple Brinkman-Kramers approximation,[8,13,14] i.e., $t_j \cong V_j$.

A. Homonuclear molecules

For homonuclear molecules, since by symmetry, $t_1=t_2=t$ for gerade state, $t_1=-t_2=t$ for ungerade state, and $\mu=\frac{1}{2}$, we have from Eq. (3)

$$T_M=t\left(e^{-i\boldsymbol{\alpha}\cdot(\boldsymbol{\rho}/2)}\pm e^{i\boldsymbol{\alpha}\cdot(\boldsymbol{\rho}/2)}\right) , \tag{7}$$

where $+$ $(-)$ stands for gerade (ungerade).

The wave function of diatomic molecule can generally be obtained by LCAO (Refs. 15–17) or other methods (cf. Secs. III B and III C). However, the complete LCAO wave functions may not be necessary when computations involve high-velocity collisions in which only inner-shell orbitals are important. Therefore we begin by representing the molecular wave function by a simple product of $1s$ hydrogenic wave functions centered at each scatterer. The spherical symmetry of $1s$ wave functions on each center allows the simplest algebra without losing the basic physics of the process. Similarly, the ionic wave function can be expressed as a sum of $1s$ hydrogenic wave functions centered on each scatterer. Thus we have for the simplest symmetrized molecular wave function Φ_M and ionic wave function Φ_i

$$\Phi_M=N_M[\psi_{1s}(1)\phi_{1s}(2)+\psi_{1s}(2)\phi_{1s}(1)] \tag{8}$$

and

$$\Phi_i=N_i^{\pm}[u_{1s}(1)\pm v_{1s}(2)] , \tag{9}$$

with

$$\begin{aligned}
N_M&=1/[2(1+\Delta_M^2)]^{1/2} ,\\
\Delta_M&=\int \psi_{1s}^*(\mathbf{r})\phi_{1s}(\mathbf{r})d\mathbf{r}\\
&=(1+Z_M\rho+\tfrac{1}{3}Z_M^2\rho^2)\exp(-Z_M\rho) ,\\
N_i^{\pm}&=1/[2(1\pm\Delta_i)]^{1/2} ,\\
\Delta_i&=\int u_{1s}^*(\mathbf{r})v_{1s}(\mathbf{r})d\mathbf{r}\\
&=(1+Z_i\rho+\tfrac{1}{3}Z_i^2\rho^2)\exp(-Z_i\rho) ,
\end{aligned} \tag{10}$$

where N_M and $N_i^{\pm}$ are normalization constants for the molecular and ionic wave functions; ψ, ϕ, u, and v are hydrogenic wave functions. Since the two atoms are identical we have ψ and ϕ (u and v) with the same form of function. The effective charge carried by molecular ψ and ϕ (ionic u and v) has been written as Z_M (Z_i) in Eq. (10). We point out that Δ_M (Δ_i) is an overlap integral of the molecular (or ionic) wave function.

In the development above we have introduced two T matrices, the molecular matrix T_M and the effective atomic matrix t. A further relationship holds for t and its atomic limit t_A which describes scattering from a free atom. Following a similar procedure to Tuan and Gerjuoy,[1] it is straightforward to show[4]

$$\begin{aligned}
\langle \Psi_b|T_M|\Psi_a\rangle=&N_MN_i^{\pm}(\Delta_{iM}\pm\chi_{iM})\\
&\times t_A\left(e^{-i\boldsymbol{\alpha}\cdot(\boldsymbol{\rho}/2)}\pm e^{i\boldsymbol{\alpha}\cdot(\boldsymbol{\rho}/2)}\right) ,
\end{aligned} \tag{11}$$

with the initial wave function $\Psi_a=e^{i\mathbf{K}_i\cdot\mathbf{R}}\Phi_M$ and the final wave function $\Psi_b=e^{i\mathbf{K}_f\cdot\mathbf{R}'}\Phi_i u'_{1s}$ in which Φ_M and Φ_i are defined in Eqs. (8) and (9), u'_{1s} is the $1s$ bound-state hydrogenic electronic wave function on the projectile. Here Δ_{iM} and χ_{iM} are overlap integrals between ionic and molecular wave functions given by[4]

$$\begin{aligned}
\Delta_{iM}&=\int u_{1s}^*(\mathbf{r})\psi_{1s}(\mathbf{r})d\mathbf{r}\\
&=8(Z_iZ_M)^{3/2}/(Z_i+Z_M)^3 ,
\end{aligned} \tag{12}$$

$$\begin{aligned}
\chi_{iM}&=\int u_{1s}^*(|\mathbf{r}-\boldsymbol{\rho}|)\psi_{1s}(\mathbf{r})d\mathbf{r}\\
&=\frac{8(Z_iZ_m)^{3/2}}{\rho\nu^3}[Z_i(\rho\nu-4Z_M)e^{-Z_M\rho}\\
&\qquad+Z_M(\rho\nu+4Z_i)e^{-Z_i\rho}] .
\end{aligned} \tag{13}$$

In Eq. (11) we have replaced the BK amplitude I_{pe} of Tuan and Gerjuoy[1] by the more general matrix t_A.

Comparing Eq. (11) with Eq. (7) we have

$$t=N_MN_i^{\pm}(\Delta_{iM}\pm\chi_{iM})t_A\equiv N_MN_iN_{iM}^{\pm}t_A\equiv N_t^{\pm}t_A . \tag{14}$$

The effective atomic matrix t differs from its atomic limit t_A by an overall constant $N_t^{\pm}$. Since $T_M=t(e^{-i\boldsymbol{\alpha}\cdot\boldsymbol{\rho}/2}\pm e^{i\boldsymbol{\alpha}\cdot\boldsymbol{\rho}/2})$ and $t=N_t^{\pm}t_A$, it is primarily $N_t^{\pm}$ that determines the difference between the molecular and twice the atomic total cross sections. By the definition above, $N_t^{\pm}$ is a constant combing the molecular wave function (N_M), the ionic wave function (N_i) and their overlap $(N_{iM}^{\pm})$, which depends on the form of the wave functions. The above expression for the overlap factor $N_{iM}^{\pm}$, derived for wave functions given by Eqs. (8) and (9), may be generalized (cf. Sec. III B).

The reflection symmetry properties of a homonuclear diatomic molecule may be used to determine $N_t^{\pm}$ under two interesting limits, i.e., the separated atom limit $(\rho\rightarrow\infty)$ and the united atom limit $(\rho\rightarrow 0)$, without specific calculations. For the limit as $\rho\rightarrow\infty$, the total normalization constant for gerade N_t^+ and ungerade N_t^- are the same. Namely, when $\rho\rightarrow\infty$, we have $N_M=N_i^+=N_i^-=(\frac{1}{2})^{1/2}$, $N_{iM}^{\pm}=1$, and $N_t^+=N_t^-=\frac{1}{2}$.

We now use the simple BK approximation[13,14] amplitude t_A^{BK}

$$t_A^{\mathrm{BK}} \cong \frac{-2^5\pi(Z_pZ_T)^{5/2}}{(Z_T^2+\alpha_o^2)^3} \tag{15}$$

in Eqs. (11) and (7), where Z_p is the charge of the projectile, Z_T is the effective charge of the nuclei in the molecule, also denoted as Z_M, to obtain

$$T_M^{\mathrm{BK}} = N_t^{\pm} t_A^{\mathrm{BK}}(e^{-i\alpha\cdot(\rho/2)} \pm e^{i\alpha\cdot(\rho/2)}) \ . \tag{16}$$

By Eq. (5), the corresponding probability amplitude a_M^{BK} is found as

$$\begin{aligned} a_M^{\mathrm{BK}} &= \frac{1}{v}\int T_M^{\mathrm{BK}} e^{i\alpha_\perp\cdot\mathbf{B}} d^2\alpha_\perp \\ &= N_t^{\pm}(a_1 e^{-i\alpha_z\rho_{z/2}} \pm a_2 e^{i\alpha_z\rho_{z/2}}) \ , \end{aligned} \tag{17}$$

where

$$\begin{aligned} a_1 &= \frac{1}{v}\int t_A^{\mathrm{BK}} e^{i\alpha_\perp\cdot\mathbf{B}_-} d^2\alpha_\perp \ , \\ a_2 &= \frac{1}{v}\int t_A^{\mathrm{BK}} e^{i\alpha_\perp\cdot\mathbf{B}_+} d^2\alpha_\perp \ , \end{aligned} \tag{18}$$

with

$$\mathbf{B}_{\pm} = \mathbf{B} \pm \rho_\perp/2 \ . \tag{19}$$

These integrals can be done analytically, namely,

$$\begin{aligned} a_1 &= -\frac{2}{v}(Z_pZ_T)^{5/2}\frac{x_-^2K_2(x_-)}{(Z_T^2+\alpha_z^2)^2} \ , \\ a_2 &= -\frac{2}{v}(Z_pZ_T)^{5/2}\frac{x_+^2K_2(x_+)}{(Z_T^2+\alpha_z^2)^2} \ , \end{aligned} \tag{20}$$

where K_2 is the Bessel function of the third kind and second order and

$$\begin{aligned} x_{\pm} &= |\mathbf{B}_{\pm}|(Z_T^2+\alpha_z^2)^{1/2} \\ &= \left[B^2 + \frac{\rho^2}{4} \pm \frac{1}{2} B\rho\cos(\phi_B - \phi_\rho) \right]^{1/2} \\ &\quad \times (Z_T^2+\alpha_z^2)^{1/2} \ , \end{aligned} \tag{21}$$

where ϕ_B and ϕ_ρ are the azimuthal directions of $\mathbf{B}$ and $\boldsymbol{\rho}$. Thus

$$\begin{aligned} a_M^{\mathrm{BK}} &= N_t^{\pm}\left[-\frac{2}{v}\frac{(Z_pZ_T)^{5/2}}{(Z_T^2+\alpha_z^2)^2} \right] \\ &\quad \times [x_-^2K_2(x_-)e^{-i\alpha_z\rho_z/2} \pm x_+^2K_2(x_+)e^{i\alpha_z\rho_z/2}] \ . \end{aligned} \tag{22}$$

The probability as a function of impact parameter is given by

$$\begin{aligned} P_M^{\mathrm{BK}}(\mathbf{B}) &= |a_M^{\mathrm{BK}}|^2 \\ &= (N_t^{\pm})^2 \left[\frac{2}{v} \right]^2 \frac{(Z_pZ_T)^5}{(Z_T^2+\alpha_z^2)^4} \\ &\quad \times [x_-^4K_2^2(x_-) + x_+^4K_2^2(x_+) \\ &\qquad \pm 2x_-^2x_+^2K_2(x_-)K_2(x_+)\cos(\alpha_z\rho_z)] \end{aligned} \tag{23}$$

The total single-capture cross section σ_M^{BK} is

$$\sigma_M^{\mathrm{BK}} = 2\int P_M^{\mathrm{BK}}(\mathbf{B})d^2B \ . \tag{24}$$

The factor of 2 comes from the indistinguishability of the two electrons. When substituting Eq. (23) into (24), σ_M^{BK} can be written as

$$\frac{\sigma_M^{\mathrm{BK}}}{2} = \sigma_1 + \sigma_2 \pm \sigma_{12} \ , \tag{25}$$

where σ_1 and σ_2 are due to individual centers and σ_{12} is due to the interference. The integrals for $\sigma_{1,2}$ in Eq. (24) can be computed analytically to give the BK cross section, i.e.,

$$\sigma_{1,2}^{\mathrm{BK}} = \frac{2^8\pi(Z_PZ_T)^5}{5v^2(Z_T^2+\alpha_o^2)^5} \ ,$$

while σ_{12} is computed numerically.

For the limit as $\rho \rightarrow \infty$, the interference term σ_{12} approach zero for both gerade and ungerade. Meanwhile, from Eq. (10), the individual terms σ_1 and σ_2 summed over gerade and ungerade give

$$\begin{aligned} \sum_{+,-}\sigma_1 = \sum_{+,-}\sigma_2 &= (N_t^+)^2\sigma_A + (N_t^-)^2\sigma_A \\ &= 2(\tfrac{1}{2})^2\sigma_A = \tfrac{1}{2}\sigma_A \ , \end{aligned}$$

thus the total cross section σ_M in Eq. (24) yields $2\sigma_A$, twice the atomic cross section. For two electrons[18] in the limit as $\rho \rightarrow 0$, again $N_t^+ \rightarrow \frac{1}{2}$, but $\cos(\alpha_z\rho_z) \rightarrow 1$ and the ungerade contribution vanishes, i.e., $N_t^- \rightarrow 0$, $Z_M \rightarrow 2Z_M$ so that $\sigma_M^{\mathrm{BK}} \underset{\rho\rightarrow 0}{\rightarrow} = 2\sigma_{UA}$. Here σ_A denotes the cross section for an isolated atom, and σ_{UA} is the 1*s*-1*s* cross section per electron for the atom with the united nuclear charge.

B. Application to H_2

The above development provides a method to calculate electron capture from homonuclear diatomic molecules using a simple, but generalizable, molecular wave function. For H_2 a somewhat better wave function is the Weinbaum wave function,[7] also used by Tuan and Gerjuoy and other authors.[1-5] Specifically, we choose

$$\begin{aligned} \Phi_M = N_M\{&\psi_{1s}(1)\phi_{1s}(2) + \psi_{1s}(2)\phi_{1s}(1) \\ &+ c[\psi_{1s}(1)\psi_{1s}(2) + \phi_{1s}(1)\phi_{1s}(2)]\} \end{aligned} \tag{26}$$

and ionic wave function

$$\Phi_i = N_i^{\pm}[u_{1s}(1) \pm v_{1s}(1)] \ , \tag{27}$$

where the normalization constant $N_i^{\pm}$ is given by Eq. (10) and N_M is given by

$$N_M = 1/\{2[(1+c^2)(1+\Delta_M^2)+4c\Delta_M]\}^{1/2} \ . \tag{28}$$

The Weinbaum wave function above differs the previous simple LCAO wave function in Eq. (8) by a bonding[15,16] term characterized by $c \neq 0$. The overlap constant $N_{iM}^{\pm}$ in this case is found[1-5] to be slightly different from that in Eq. (14), namely,

$$N_{iM}^{\pm} = (\Delta_{iM} \pm \chi_{iM})(1 \pm c) \ . \tag{29}$$

The form of Eqs. (7) and (14) is not changed. If we take the bonding term $c \rightarrow 0$, then $N_{iM}^{\pm}$ reduces to the simpler form in Eq. (14). For H_2 at equilibrium, we use $\rho = 1.4$, $Z_M = 1.193$, $c = 0.256$, and $Z_i = 1.4$.

C. Heteronuclear diatomic molecules

For heteronuclear diatomic molecules we again choose a simple LCAO wave function with only s wave contributions. Now we use 1 and 2 to denote the electrons, and A and B to denote the two different atomic nuclei. The molecular wave function is given by[15]

$$\phi_M = N_M[a u_{MA}(1) + b u_{MB}(1)][a u_{MA}(2) + b u_{MB}(2)] , \tag{30}$$

where

$$N_M = [(a^4 + b^4) + 2a^2 b^2 (1 + 2\Delta_M^2) + 4ab(a^2 + b^2)\Delta_M]^{-1/2} . \tag{31}$$

Here $\Delta_M = \int u_{MA}^*(1) u_{MB}(1) d\tau_1$ and, for example,

$$u_{MA,B} = \frac{(Z_{A,B})^{3/2}}{\sqrt{\pi}} \exp(-Z_{A,B} r) .$$

The ionic wave function is given by

$$\phi_i = N_i[a' u_{iA}(2) + b' u_{iB}(2)] , \tag{32}$$

with $N_i = [(a')^2 + (b')^2 + 2a'b'\Delta_i]^{-1/2}$ and $\Delta_i = \int u_{iA}^* u_{iB} d\tau$. Using these wave functions, it is straightforward to show that to an overall phase

$$T_M \cong T_A + T_B e^{i\alpha\cdot\rho} , \tag{33}$$

where it is convenient to choose the origin at the center of mass of the molecule. The mathematical evaluation of prabability amplitudes is now similar to the homonuclear case, which is recovered as $a \rightarrow b$ and $a' \rightarrow b'$, corresponding to $c = 1$ in Eq. (26).

Although the algebra is quite similar for the homonuclear and heteronuclear cases, the identification of final states and counting of electrons is a little different. If $A \neq B$ in molecule AB, then A^+B is a different final state than AB^+. Thus T_A differs from T_B. At the same time gerade and ungerade labels no longer apply since there is no reflection symmetry. We also note that for most diatomic molecules there are four electrons in the ground state, twice as many as in H_2. Hence, except for two-electron systems like H_2, $\sigma_M \xrightarrow[\rho\rightarrow 0,\infty]{} 2(\sigma_A + \sigma_B)$ where $\sigma_{A,B}$ is a 1s atomic cross section per electron for center A and B.

IV. RESULTS AND DISCUSSION

A. Results for H_2

1. Orientation dependence of P(**B**)

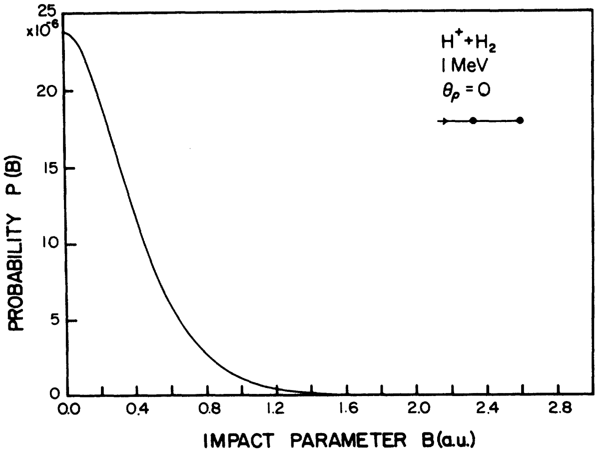

FIG. 3. Capture probability $P(\mathbf{B})$ as a function of impact parameter B. When $\theta_\rho = 0$, the beam passes through the molecular axis, therefore $P(\mathbf{B})$ is independent of ϕ_ρ.

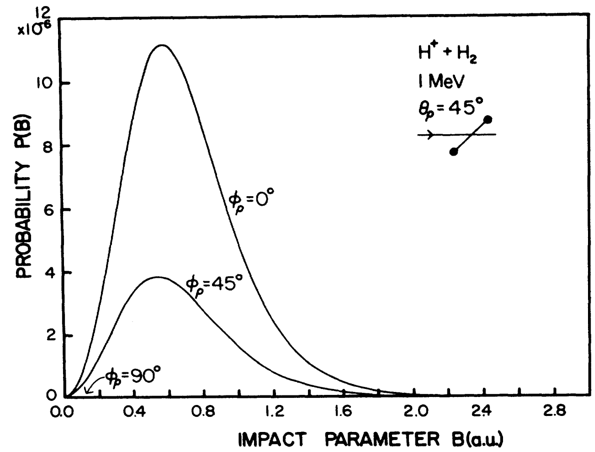

FIG. 4. Capture probability $P(\mathbf{B})$ as a function of impact parameter B when $\theta_\rho = 45°$ and ϕ_ρ is varied. We note when $\phi_\rho = 90°$, $P(\mathbf{B})$ (not shown) is very small but peaked at $B = 0$.

Capture probabilities $P(\mathbf{B})$ as a function of impact parameter B, for capture from a target gerade ground state to a 1s projectile ground state, are shown in Figs. 3, 4, and 5 for fixed orientations of the molecular axis at θ_ρ and $\phi_\rho = 0°$, 45°, and 90°. The ϕ dependence depends on $\phi_B - \phi_\rho$. In these graphs, the scattering plane has been fixed at $\phi_B = 0$ and taken as the reference plane for both angles. The orientation dependence can usually be explained by the following physical picture. The most probable beam position for electron capture is the position closest to the most densely populated charge cloud, e.g., near the nuclei. For the case of $\phi_\rho = 0°$, the molecule lies on the scattereing plane. Therefore the impact parameter at which the probability maximizes yields the value $s = \rho_\perp/2 = (\rho/2)\sin\theta_\rho$, which is the perpendicular distance between the incident beam and the center of the H_2 molecule. Figures 3, 4, and 5 show that the peaks usually occur at this distance s. In Fig. 4 for $\theta_\rho = 45°$, the $\phi_\rho = 0°$, 45° curves are shifted somewhat because of the

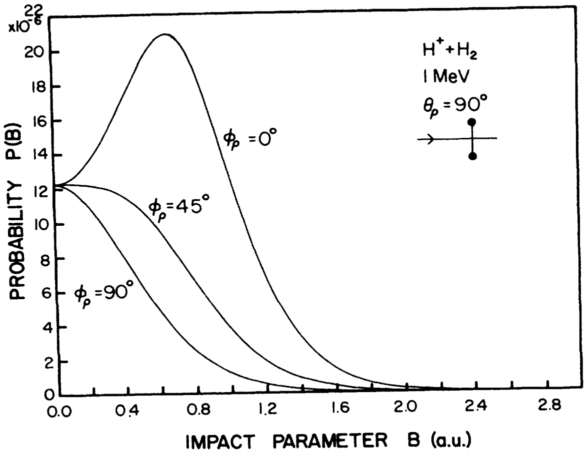

FIG. 5. Capture probability $P(\mathbf{B})$ as a function of impact parameter B when $\theta_p=90°$ and ϕ_p is varied.

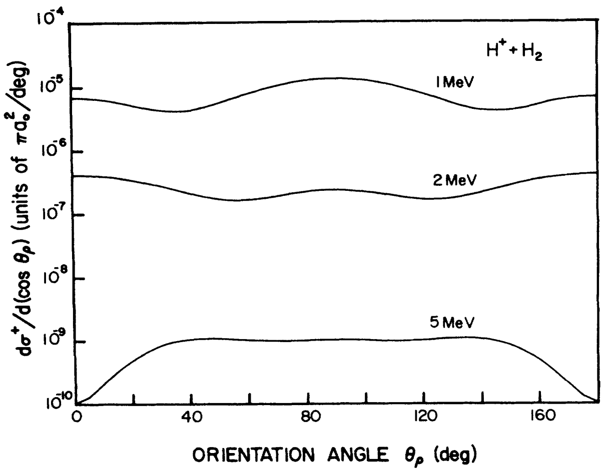

FIG. 6. Single-capture cross sections summed over ϕ_p as a function of θ_p. The cross section is symmetric about $\theta_p=90°$. At 5 MeV there is almost an order of magnitude difference between $\theta_p=0$ and $40° < \theta < 140°$. These differences fluctuate with energy of the projectile. Minimums at $\theta_p=0$ occur when $\delta=\alpha_z\rho_z=(2n+1)\pi$ $(n=0,1,2,3,\ldots)$.

near zero probability at the zero impact parameter. The zero probability is caused by the particular phase value that contributes to destructive interference at $B=0$. The phase is close to π when $E=1$ MeV, $\theta_p=45°$, and $\phi_p=0$ since $\alpha_z\rho_z \cong (v/2)\rho\cos\theta_p=3.13$. One may expect similar destructive interference at zero impact parameter whenever the phase equals $(2n+1)\pi$ $(n=0,1,2,\ldots)$.

Although for $\phi_p=0°$ all cases shown seem to be well explained by electrons located at separate centers, some cases for $\phi_p \neq 0°$ are more complicated since the electrons actually are not well localized at the two centers. Since ϕ_p plane and ϕ_B plane no longer coincide, the dependence on ϕ_p sometimes becomes stronger than on θ_p. These figures suggest a competition between the two angles. At $\theta_p=90°$, for example, the identification of an isolated center becomes impossible.

2. *Orientation dependence of cross sections*

Knowing there is an orientation dependence in the probability one may anticipate that an orientation dependence in the cross section exists as well. Figures 6 and 7 document the orientation dependence which results from the interference between amplitudes from each of the two centers. In these figures, cross sections have been summed over ϕ_B keeping θ_p fixed. Since the cross sections depend on $\phi_B-\phi_p$, summing over ϕ_B removes the dependence on ϕ_p.

In Fig. 6 the single capture cross section for $p+\mathrm{H}_2$ collision is illustrated for impact energies of 1, 2, and 5 MeV. The ungerade cross sections, typically a few percent of the gerade cross sections, are not shown. The orientation dependence at these different energies varies drastically. At 1 MeV, the peak of the oscillation is about factor of 2 larger than the valley. However, the 2 MeV graph shows relatively small oscillations with the orientational angles. The cross sections at 5 MeV have the biggest difference between the maxima and minima, although the cross section tends to be flat over a broad range of orientational angles. The orientation dependence is caused by the phase term $\delta=\alpha_z\rho_z$, which contributes to all the patterns in these figures. The value of phase at different orientational angles will determine whether interference is constructive or destructive. The phase δ is obviously zero for any projectile energy at $\theta_p=90°$. Therefore, at $\theta_p=90°$, interference is always constructive. It is also possible to find other angles that yield phase values equal to $2n\pi$, thus contributing constructively. At $\theta_p=0$, the phase acquires different values for different energies. For instance, for 1-MeV projectiles, the phase is approximately 1.4π at $\theta_p=0$ and for 2 MeV the phase is about 2π at $\theta_p=0$. At 5 MeV, the phase is roughly 3π, so that a minimum occurs at $\theta_p=0$.

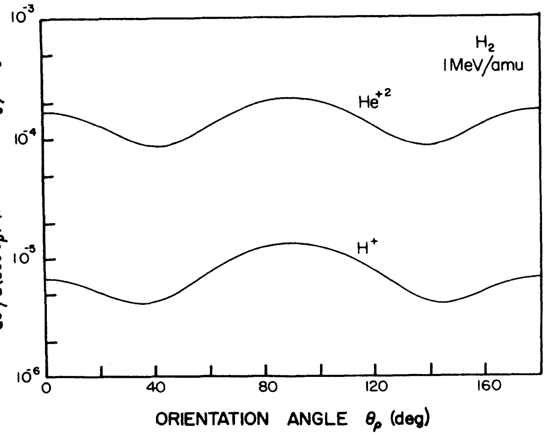

FIG. 7. Single-capture cross sections summed over ϕ_p as a function of θ_p for proton and α particles colliding with H_2 at the same incident velocity. The interference effect decreases somewhat as the projectile charge increases.

Such a minimum occurs at any energy where $\alpha_z\rho_z=(2n+1)\pi$. The total cross sections, obtained by summing over all orientations, are found to be in good agreement with results of quantum-mechanical wave treatment.[3]

In Fig. 7 we show the cross section versus θ_p for projectiles of different charge state Z_p. Specifically, we present result for H^+ and He^{2+} at same incident velocity. The θ_p dependence in our calculations is approximately independent of Z_p at a fixed collision velocity v because the phase $\delta=\alpha_z\rho_z$ is independent of Z_p when $\Delta E/v \ll v/2$.

B. Discussion

While the impact-parameter treatment and the quantum-mechanical wave treatment give the same physical observables such as cross sections, the conceptual pictures differ, as may be seen by comparing Figs. 1 and 2. For a symmetric molecule such as H_2 in the wave picture the net flux at a scattering angle is simply the flux from either center modified by a factor of $|2\cos[\boldsymbol{\alpha}\cdot(\boldsymbol{\rho}/2)]|^2$. In the impact-parameter picture the net probability is the sum of the probability for scattering from each center plus an interference term proportional to $\cos(\alpha_z\rho_z)$. In both cases, if the separation between the two atomic centers become large, i.e., $\rho\rightarrow\infty$, then the interference terms average to zero, and total cross sections are sum of the cross sections from each center.

A central result of this paper is that the probability amplitudes a_1 and a_2 from each center differ by a phase $\alpha_z\rho_z$ due to the displacement $\boldsymbol{\rho}$ of the two centers. This result has very recently been verified by Lin and Shingal[19] by combining a translation factor $e^{i\mathbf{v}\cdot\boldsymbol{\rho}}$ with the difference in the transit time of the projectile. The overall phase term δ could depend on any energy change ΔE or a time change Δt, or both. In our development δ arises from energy considerations in a time-independent picture while Lin and Shingal obtain the same phase from time dependence on an energy invariant picture. The Lin-Shingal derviation entirely avoids reference to the amplitude in the wave picture.

We have invoked several approximations in this paper. First we have ignored rescattering terms in Eq. (1) and used $T_M\cong T_1+T_2$. Within the first Born approximation this is correct. If higher Born terms are significant, e.g., if collision velocities are near or below 25 KeV/amu for H_2, then these rescattering terms may also become non-negligible. Here, for simplicity, we have used the first Born Brinkman-Kramers[8] approximation. It is well known that the total cross sections are a factor of 3 or more too large in the BK approximation. Use of a boundary corrected first Born approximation[20-25] would probably give more accurate total cross sections. The $\cos(\alpha_z\rho_z)$ interference terms, which determine the orientation dependence of our cross sections, are independent of the approximation used for T_1 and T_2 in Eq. (1). Hence we do not expect the orientation dependence of our results to change if different approximations are used for T_1 and T_2, unless those approximations introduce a phase difference between T_1 and T_2.

The molecular wave functions have also been approximated in our calculations. We have only included the simplest s wave terms in our development. It is, however, well known that more exact LCAO wave functions contain[15-17] non-s-wave contributions. These contributions may alter the form of Eq. (11) when a more exact T matrix containing various partial waves is Fourier transformed.

We have also ignored effects due to the internuclear trajectory in our development. Such an effect could be included by incorporating an internuclear phase $\delta_N=\int V_N dz$, following, for example, the earlier work of Rogers and McGuire.[26] We expect these nuclear phase contributions to become very small at high collision velocities since $\delta_N=\int V_N dt=1/v\int V_N dz$. However, it may be that these terms are non-negligible compared to the $\Delta E/v$ terms originating from α_z. That is, the δ_N phase terms could be significant in excitation and ionization.

One motivation for evaluating $P(\mathbf{B})$ is that $P(\mathbf{B})$ may normally be used to find cross sections for double capture. Within the independent electron approximation,[27] ignoring electron symmetry, the probability for capturing two electrons is P_1P_2, where P_1 and P_2 are the probabilities for capture of electron 1 and 2, respectively. However, for indistinguishable electrons as in H_2, there is difficulty.[28] Following Eq. (6) let $a_M=(a_1+a_2e^{i\delta})$ be the probability amplitude for single capture of either electron. Then the probability for capturing both electron is

$$|a_M|^2|a_M|^2=[|a_1|^2+|a_2|^2\,\mathrm{Re}(a_1a_2e^{i\delta})]^2\ .$$

As $\rho\rightarrow\infty$, the interference term $2\,\mathrm{Re}(a_1a_2e^{i\delta})$ can be dropped, but $|a_1|^2$ and $|a_2|^2$ remain finite. Hence we obtain a finite probability for double electron capture in a single collision from well-isolated atomic hydrogen atoms. This present a difficulty since the probability for double capture should decrease as ρ becomes large, e.g., as $|a_1|^2|a_2|^2$ and not $|a_1|^4$ or $|a_2|^4$. Our conclusion is that the independent electon approximation for double capture in the symmetric diatomic molecule H_2 needs further study incorporating[29] the identical nature of the electrons.

The orientation dependence of total cross sections for scattering from diatomic molecules of a given orientation depends on $\alpha_{\min}$, the minimum value of the momentum transfer of the projectile. For ionization,[30] one may follow a similar development with $\alpha_{\min}=\Delta E/v=(I+1/2k^2)$, where $\frac{1}{2}k^2$ is the kinetic energy of the ejected electron and I is the ionization energy. Most of the ionization cross sections sum over all ejected electron energies. If $\alpha_{\min}\rho_z\gg 1$, e.g., $(I+1/2k^2)\rho_z/v\gg 1$, then the interference terms tend to average out and there could be little orientation dependence for ionization. For capture and excitation $\alpha_{\min}$ is fixed and the interference and orientation effects may be more distinct than ionization.

V. SUMMARY

We have formulated the probability amplitude for scattering from diatomic molecules at high collision velocities ignoring rescattering between the atomic centers. Probabilities and cross sections have been evaluated for fixed orientation of the molecular axis. For electron capture from H_2 by protons at about 1 MeV the cross section varies by more than a factor of 2 for different orientations of the molecular axis. The orientation dependence, which could be observed experimentally, is described by an interference of scattering amplitudes from the atomic centers of the molecule.

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