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Electron transfer and spin-flip processes in atom-atom collisions from variationally improved time-dependent Hartree-Fock results

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A variational functional for transition amplitudes is applied to atom-atom collisions using a time-dependent formalism. The transition amplitude is a functional of two independent trial wave functions with specified initial and final conditions, respectively. Transition probabilities are obtained by evaluating the functional in terms of standard time-dependent Hartree-Fock (TDHF) trial functions. The TDHF method is implemented by expanding the molecular orbitals as linear combinations of traveling atomic orbitals. The procedure requires no other molecular integrals than those needed to construct the Fock operator. The present method is applied to $\mathrm{He}+\mathrm{He}^{2+}$ and $\mathrm{H}^{+}+\mathrm{He}^{+}$ collisions with specified nuclear trajectories using a minimal atomic-orbital basis set. Within this model an exact, close-coupling-type solution is also feasible, and has been obtained for comparison purposes. Numerical values of probabilities and of cross sections obtained from the variational functionals for elastic, spin-flip, and one- and two-electron transfer processes show substantial improvements over the standard TDHF results.

I. INTRODUCTION

In the many-electron theory of atomic collisions, a possible way of describing electronic energy or charge-transfer processes is to allow the individual electronic states to evolve in time under the influence of the other electrons and of the nuclear dynamics.

The physical picture, that each electron moves in a time-dependent average field, suggests implementing the time-dependent Hartree-Fock (TDHF) approximation. A variational derivation of the TDHF equations was first given by Dirac,[1] and later in a more general form by Frenkel,[2] whose variational principle has been extensively discussed by many authors.[3-7] The TDHF theory has long been applied to atomic and molecular structure calculations in a perturbative form,[8-10] and is also known as the random-phase approximation with exchange.[11-13]

In recent years the TDHF theory has also been successfully applied to atomic[14] and molecular[15] collisions by solving the TDHF equations in the coordinate representation. Stich *et al.*[16] presented the first results of a basis-set expansion for atomic collisions. In the TDHF approach the many-electron wave functions of the colliding system are written as antisymmetrized products of molecular orbitals. Transition amplitudes are then calculated by projecting the Hartree-Fock (HF) wave function, evolved from a specified initial state, at the final time onto a given final HF state. This standard procedure, however, might be rather inaccurate since the error of the wave function appears in first order in the transition probabilities. Moreover, time reversibility is not necessarily satisfied.

To overcome these difficulties, Demkov[17] constructed a variational functional whose stationary value directly gives the transition amplitude. In Demkov's method the transition amplitude is a functional of both the forward and the backward evolving trial wave functions with fixed initial and final conditions, respectively. Recently, different functionals have been used[18,19] to derive the corresponding Euler-Lagrange equations for the wave functions. These equations can be solved only by iteration, and are similar in nature to the equations obtained via a functional-integration technique used in nuclear physics.[20]

In the present work we apply the variational-functional method developed in Ref. 21 to calculate state-to-state transition probabilities and cross sections within a realistic model of atom-atom collisions. The method employs only standard TDHF wave functions, restores microscopic reversibility, and improves accuracy. This is a detailed version of a previous paper[22] that contained preliminary results.

The organization of this paper is as follows. Section II contains a discussion of a semiclassical description of atom-atom collisions followed by the introduction of the transition-amplitude functional. In Sec. III we present the TDHF formalism using a basis-set expansion. We describe our model and derive the corresponding equations for helium and helium-ion collisions in Sec. IV. Features of our numerical procedure and results constitute Sec. V. Finally, the conclusions and some comments can be found in Sec. VI.

II. ATOM-ATOM COLLISIONS

A. Time-dependent treatment

Let us consider a colliding two-center (a and b), two-electron system, where a and b refer to two nuclei with masses m_a and m_b, respectively. The corresponding space-fixed coordinate system is shown in Fig. 1. Selecting $\mathbf{R}$, $\mathbf{r}_1$, and $\mathbf{r}_2$ as independent variables, the total Hamiltonian $\mathcal{H}$ of the system is (in atomic units, $\hbar=1$)

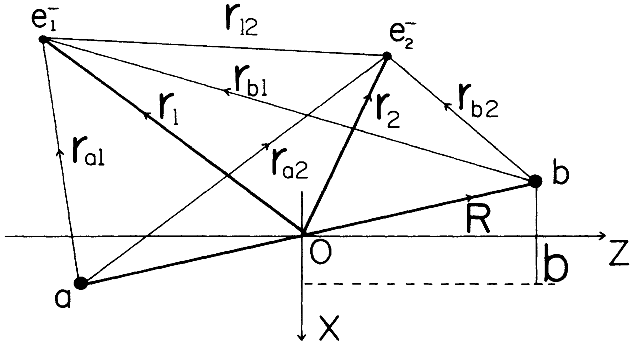

FIG. 1. Reference frame for a colliding two-electron–two-center system.

$$\mathcal{H}=-\frac{1}{2M}\left[\frac{\partial}{\partial \mathbf{R}}\right]^2+V_{ab}+\sum_{j=1}^{2}\left[-\frac{1}{2}\left[\frac{\partial}{\partial \mathbf{r}_j}\right]^2+\sum_{n=a,b}V_{nj}\right]+v_{12}\ , \tag{2.1}$$

where M is the reduced mass of the two nuclei, $V_{ab}(R)$ is the nuclear repulsive potential, $V_{nj}(r_{nj})$ is the electron-nucleus interaction, and $v_{12}=1/r_{12}$. The potential V_{nj} depends on the coordinates $\mathbf{R}$ and $\mathbf{r}_j$, through

$$\begin{aligned}&\mathbf{r}_{aj}=\mathbf{r}_j-q_a\mathbf{R}\ ,\\&\mathbf{r}_{bj}=\mathbf{r}_j+q_b\mathbf{R}\ ,\\&q_a+q_b=1\ ,\end{aligned} \tag{2.2a}$$

where

$$q_n=M/m_n,\quad n=a,b \tag{2.2b}$$

corresponds to the choice when the origin of the coordinate system, O, is at the center of masses of the two nuclei.

We note here that a and b can refer, without loss of generality, to two ion cores. In this case V_{ab} and V_{nj} are suitably chosen effective potentials.

The total wave function Ψ satisfies the time-independent Schrödinger equation

$$(\mathcal{H}-E)\Psi(\mathbf{x}_1,\mathbf{x}_2;\mathbf{R})=0\ , \tag{2.3}$$

where E is the total energy, and x_j stands for $(\mathbf{r}_j,\zeta_j)$, ζ_j being the spin variable of the jth electron.

Since we are primarily interested in high-energy ($E\sim$keV) collisions, we adopt in the following the impact-parameter approach.[23] The impact-parameter method makes explicit use of the fact that at sufficiently high energies, scattering takes place mainly in the forward direction within an angle of a few degrees. It suggests that we write

$$\Psi=\exp(i\mathbf{k}\cdot\mathbf{R})\Phi(\mathbf{x}_1,\mathbf{x}_2;\mathbf{R})\ , \tag{2.4a}$$

where $\mathbf{k}$ is the wave vector of the relative motion in the direction of incidence with magnitude

$$k=(2ME)^{1/2}\ . \tag{2.4b}$$

Substituting Eq. (2.4a) in the Schrödinger equation (2.3), we obtain

$$-\frac{1}{2M}\left[\left[\frac{\partial}{\partial \mathbf{R}}\right]^2+2i\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{R}}\right]\Phi+H\Phi=0\ , \tag{2.5}$$

where

$$H=\sum_{j=1}^{2}\left[-\frac{1}{2}\left[\frac{\partial}{\partial \mathbf{r}_j}\right]^2+\sum_{n=a,b}V_{\mu j}\right]+v_{12}+V_{ab} \tag{2.6}$$

is the electronic Hamiltonian. Provided $\Phi(\mathbf{x}_1,\mathbf{x}_2;\mathbf{R})$ is a smoothly varying function of $\mathbf{R}$, and provided k is large, one can safely assume that

$$\left|\left[\frac{\partial}{\partial \mathbf{R}}\right]^2\Phi\right|\ll\left|\mathbf{k}\cdot\frac{\partial}{\partial \mathbf{R}}\Phi\right|\ , \tag{2.7}$$

and that the first term in Eq. (2.5) is negligible. Introducing the time variable t, via $\mathbf{k}=Md\mathbf{R}/dt$, so that

$$\mathbf{R}(t)=\mathbf{b}+\mathbf{v}t,\quad \mathbf{b}\cdot\mathbf{v}=0\ , \tag{2.8}$$

where $\mathbf{b}$ is the impact-parameter vector (see Fig. 1) and $\mathbf{v}=\mathbf{k}/M$ is the relative velocity, Eq. (2.6) can be written in the form

$$\{i(\partial/\partial t)_{\text{SF}}-H[\mathbf{R}(t)]\}\Phi(\mathbf{x}_1,\mathbf{x}_2;t)=0\ , \tag{2.9}$$

where we have explicitly indicated that the partial time derivative must be taken while keeping the electronic coordinates $\mathbf{r}_j$ fixed in the reference frame O. Equation (2.9) is the time-dependent Schrödinger equation written in a space-fixed (SF) coordinate system that describes the electronic motion within the semiclassical impact-parameter approximation. A rigorous, and more physical, eikonal approach, allowing a consistent coupling between the classical nuclear and quantal electronic motion, can be found in Ref. 24.

B. The transition-amplitude functional

Let us suppose that we have found the approximate solutions, $\Phi_i^{(+)}(t)$ and $\Phi_f^{(-)}(t)$, of Eq. (2.9) which satisfy specified conditions at the initial time, t_1, and at the final time, t_2, respectively, i.e.,

$$\Phi_i^{(+)}(t_1)=\Phi_i^{(1)}\ , \tag{2.10a}$$

$$\Phi_f^{(-)}(t_2)=\Phi_f^{(2)}\ . \tag{2.10b}$$

The transition amplitudes,

$$S_{fi}^{(+)}=\langle\Phi_f^{(2)}\,|\,\Phi_i^{(+)}(t_2)\rangle\ , \tag{2.11a}$$

$$S_{fi}^{(-)}=\langle\Phi_f^{(-)}(t_1)\,|\,\Phi_i^{(1)}\rangle\ , \tag{2.11b}$$

determine the state-to-state transition probabilities

$$P_{fi}^{(\pm)}=|S_{fi}^{(\pm)}|^2\ . \tag{2.12}$$

One can see that, if the approximate wave functions $\Phi^{(\pm)}(t)$ differ from the exact ones by a quantity $\delta\Phi^{(\pm)}(t)$, the probabilities as given by Eq. (2.12) will contain an error of first order in $\delta\Phi^{(\pm)}(t_\pm)$, where $t_+=t_1$ and $t_-=t_2$.

Furthermore, microscopic reversibility may be lost, i.e., $P_{fi}^{(+)} \neq P_{fi}^{(-)}$.

To overcome these shortcomings, in Ref. 21 we defined the transition amplitude as the stationary value of the following functional:

$$\mathcal{S}_{fi}[\Phi_i^{(+)},\Phi_f^{(-)}] = \mathcal{S}^{(1)}[\Phi_i^{(+)},\Phi_f^{(-)}] + \mathcal{S}^{(2)}[\Phi_i^{(+)},\Phi_f^{(-)}] \ , \tag{2.13}$$

in which

$$\mathcal{S}^{(1)} = \frac{1}{2}\left[\langle \Phi_f^{(-)} \mid \Phi_i^{(+)} \rangle_{t_2} \exp\left[-i \int_{t_1}^{t_2} dt\, \Delta^{(+)}(t)\right] + \langle \Phi_f^{(-)} \mid \Phi_i^{(+)} \rangle_{t_1} \exp\left[-i \int_{t_1}^{t_2} dt\, \Delta^{(-)}(t)\right]\right] , \tag{2.14a}$$

$$\mathcal{S}^{(2)} = -\frac{i}{2} \int_{t_1}^{t_2} dt \exp\left[-i \int_{t_1}^{t} dt' \Delta^{(+)}(t') + i \int_{t_2}^{t} dt' \Delta^{(-)}(t')\right] [\langle \Phi_f^{(-)} \mid (\mathcal{D} - \Delta^{(+)}) \Phi_i^{(+)} \rangle + \langle (\mathcal{D} - \Delta^{(-)}) \Phi_f^{(-)} \mid \Phi_i^{(+)} \rangle] , \tag{2.14b}$$

where

$$\Delta^{(+)} = \langle \Phi_i^{(+)} \mid \mathcal{D} \Phi_i^{(+)} \rangle \ , \qquad \Delta^{(-)} = \langle \mathcal{D} \Phi_f^{(-)} \mid \Phi_f^{(-)} \rangle \ , \tag{2.14c}$$

$$\mathcal{D} \equiv H - i(\partial/\partial t) \ , \tag{2.14d}$$

and the wave functions $\Phi^{(\pm)}$ are assumed to be normalized. The right-hand side of Eq. (2.14a) is the average of the transition amplitudes obtained by the standard projection procedure of Eqs. (2.11) with a specific choice for the phases of the trial wave functions $\Phi^{(\pm)}$. $\mathcal{S}^{(2)}$, in Eq. (2.14b), is a variational contribution to the total scattering amplitude, $\mathcal{S}_{fi}$, which has the following properties:[21] (1) It is independent of the phases of the $\Phi^{(\pm)}$'s; (2) its first variation is of second order in $\delta\Phi^{(\pm)}$; (3) it satisfies microscopic reversibility; and (4) it gives the exact transition amplitudes if $\Phi_i^{(+)}$ or $\Phi_f^{(-)}$ is the exact solution of the Schrödinger equation (2.9). In this latter case $\Delta^{(\pm)}(t) \equiv 0$, and $\mathcal{S}^{(2)} = 0$.

The idea of defining the transition amplitude by a variational functional which has the same properties as described above is not new. For example, Demkov[17] defined the transition amplitude as the stationary value of the following functional:

$$\mathcal{S}'_{fi} = \langle \Phi_f^{(-)} \mid \Phi_i^{(+)} \rangle_{t_2} \exp\left[-i \int_{t_1}^{t_2} \frac{\langle \Phi_f^{(-)} \mid \mathcal{D} \Phi_i^{(+)} \rangle}{\langle \Phi_f^{(-)} \mid \Phi_i^{(+)} \rangle} dt\right] , \tag{2.15}$$

Equation (2.15) was derived in Ref. 17 by using a two-step variational procedure; later it was rederived in a more direct way by Blaizot and Ripka[18] employing a modified functional.

However, there is a pitfall in this method if one wants to obtain transition amplitudes by evaluating $\mathcal{S}'_{fi}$, in Eq. (2.15) for given approximate wave functions. Namely, the overlap $\langle \Phi_f^{(-)}(t) \mid \Phi_i^{(t)}(t) \rangle$ in the integrand of the right-hand side of Eq. (2.15) may become zero or extremely small at some points between t_1 and t_2, hence resulting in meaningless probabilities. In the following parts of this paper we wish to apply the variational expression of Eqs. (2.13) and (2.14) to calculate improved state-to-state transition probabilities and cross sections for electronic rearrangement processes in atom-atom collisions, using the standard TDHF wave functions, $D^{(\pm)}$, as approximate solutions to Eqs. (2.9).

III. THE HARTREE-FOCK APPROXIMATION

A. Molecular orbitals

A possible way of obtaining approximate solutions to Eq. (2.9) is to implement the time-dependent Hartree-Fock method. The TDHF equations can be derived from the Frenkel variational principle[2]

$$\langle \delta D \mid [H - i(\partial/\partial t)] D \rangle + \text{c.c.} = 0 \ , \tag{3.1}$$

by employing a determinantal trial function D in the form

$$D(\mathbf{x}_1,\mathbf{x}_2;t) = 2^{1/2} \mathcal{A} \psi_1(\mathbf{x}_1;t) \psi_2(\mathbf{x}_2;t) \ , \tag{3.2}$$

containing, in the two-electron case, two spin orbitals ψ_j, $j=1,2$, which should satisfy the orthonormality requirement

$$\langle \psi_i \mid \psi_j \rangle = \delta_{ij} \ . \tag{3.3}$$

In Eq. (3.2) $\mathcal{A}$ is the antisymmetrizing projection operator.

The spin orbitals ψ_j are generated by taking the internuclear axis $\mathbf{R}$ as the axis of quantization, i.e., they are given in a body-fixed frame (BF). In Eq. (3.1), however, $\partial/\partial t$ is defined in a space-fixed coordinate system [cf. Eq. (2.9)]. Taking the xz plane as the plane of scattering, the time derivative in Eq. (3.1) can be transformed to the body-fixed frame in accordance with

$$(\partial/\partial t)_{\text{SF}} \psi_j^{(\text{BF})} = [(\partial/\partial t)_{\text{BF}} - i\omega_y L_y] \psi_j^{(\text{BF})} \ , \tag{3.4}$$

where ω_y is the angular velocity ($= bv/R^2$ for a constant velocity v), and L_y is the y component of the orbital angular momentum operator in the rotating (BF) frame.[14(c),23]

Substituting the HF trial function of Eq. (3.2) into Eq. (3.1) and taking into account Eq. (3.4), we obtain the TDHF equations (and the complex-conjugate equations):

$$[F_1 + V_L - i(\partial/\partial t)_{\text{BF}}] \psi_j(\mathbf{x}_1;t) = 0, \quad j = 1,2 \ , \tag{3.5}$$

in the body-fixed frame, where F_1 is the nonlocal Fock operator given by

$$F_1(t) = -\frac{1}{2}\left[\frac{\partial}{\partial \mathbf{r}_1}\right]^2 + \sum_n V_{n1} + \sum_{j=1}^{2} \langle \psi_j \,|\, v_{12}(1-P_{12})\psi_j \rangle_2 \ , \tag{3.6}$$

where P_{ij} is the permutation operator. The term $V_L = -\omega_y L_y$ in Eq. (3.5) is the Coriolis coupling due to frame rotation.

B. Linear combination of traveling atomic orbitals

The spin orbitals ψ_j in Eq. (3.2) are written as

$$\psi_j(\mathbf{x}_i;t) = \phi_j(\mathbf{r}_i;t)\eta_j(\zeta_i) \ , \tag{3.7}$$

where $\phi_j(\mathbf{r}_i;t)$ is the jth time-dependent molecular orbital (MO) at the position of the ith electron, and $\eta_j(\zeta_i)$ is the corresponding spin function. In the asymptotic region $(R \rightarrow \infty)$, Φ, the solution of Eq. (2.9), can be expressed at fixed nuclear positions in terms of one-electron or two-electron atomic wave functions. The one-electron, hydrogenlike wave functions χ_μ satisfy the equation

$$\left[-\frac{1}{2}\left[\frac{\partial}{\partial \mathbf{r}_{nj}}\right]^2 + V_{nj} - \varepsilon_\mu\right]\chi_\mu(\mathbf{r}_{nj}) = 0 \ , \tag{3.8}$$

where $\mathbf{r}_{nj} = \mathbf{r}_j - q_n \mathbf{R}$, χ_μ, with $\mu = (n,\lambda)$ is the λth eigenfunction of the one-electron atom n with eigenenergy ε_μ. In the case when both electrons are around the same nucleus at infinite separation of the two nuclei, the asymptotic form of Φ can only be given approximately. It is usually constructed from the atomic orbitals χ_μ, defined by Eq. (3.8). However, when the nuclei are moving, Φ must be built up from traveling atomic eigenfunctions,[25] ξ_μ:

$$\xi_\mu = \chi_\mu(\mathbf{r}_{nj})\exp[i\alpha_n(\mathbf{r}_j;t)] \ , \tag{3.9a}$$

$$\alpha_n = \mathbf{v}_n \cdot \mathbf{r}_j - v_n^2 t/2 \ . \tag{3.9b}$$

Here

$$\mathbf{v}_n = q_n \mathbf{v}, \quad \text{when } n = a$$

$$= -q_n \mathbf{v}, \quad \text{when } n = b \ ,$$

and χ_μ is the solution of Eq. (3.8). The traveling wave functions ξ_μ satisfy the following differential equation:

$$\left[-\frac{1}{2}\left[\frac{\partial}{\partial \mathbf{r}_j}\right]^2 + V_{nj} - \varepsilon_\mu - i\frac{\partial}{\partial t}\bigg|_{\mathrm{SF}}\right]\xi_\mu(\mathbf{r}_{nj};t) = 0 \ . \tag{3.10}$$

It is easy to verify that if the initial conditions for Φ, in Eq. (2.9), are properly constructed from traveling atomic eigenfunctions as given by Eq. (3.9), the transition probabilities, obtained from the asymptotic solutions of Eq. (2.9), are independent of the choice of the coordinate system, i.e., of the particular choice of q_n, and, consequently, no spurious asymptotic couplings occur.

One can attempt to solve Eq. (3.5) by expanding the MO's in a basis of normalized but not necessarily orthogonal traveling atomic orbitals (TAO's) $\xi_\mu(\mathbf{r}_{ni};t)$:

$$\phi_j = \sum_{n=a,b}\sum_{\mu=1}^{M_n} c_{\mu j}(t)\xi_\mu(t) \ , \tag{3.11}$$

where the c's are complex linear combination coefficients to be determined, and M_n is the number of TAO's centered around nucleus n in the expansion.

In the space of atomic states $\xi_\mu(\mathbf{r}_{ni})\eta_j(\zeta_i)$ the TDHF equation (3.5) becomes

$$i\underline{S}(d/dt)\underline{c}_j = (\underline{F} + \underline{V}_L - i\underline{\Omega})\underline{c}_j, \quad j = 1,2 \ , \tag{3.12}$$

where the complex, Hermitian $(M_a + M_b)$-dimensional square matrices $\underline{F}$, $\underline{V}_L$, and $\underline{S}$ are the Fock, Coriolis, and overlap matrices, respectively; $\underline{\Omega}$ is given by its elements

$$\Omega_{\mu\zeta,\mu'\zeta'} \equiv \langle \xi_\mu \,|\, (\partial/\partial t)_{\mathrm{BF}}\xi_{\mu'} \rangle \delta_{\zeta\zeta'} \ ; \tag{3.13}$$

and $\underline{c}_j$ is a column vector with elements $c_{\mu j}$. The matrix multiplying $\underline{c}_j$ on the right-hand side of Eq. (3.12) is obviously non-Hermitian. Nevertheless, from Eq. (3.12) and from its adjoint, it follows that, temporarily omitting the subscript j,

$$\frac{d}{dt}N^2 \equiv \frac{d}{dt}(\underline{c}^\dagger \underline{S}\,\underline{c}) = \underline{c}^\dagger\left[\frac{d}{dt}\underline{S} - \underline{\Omega} - \underline{\Omega}^\dagger\right]\underline{c} \ . \tag{3.14}$$

But since

$$\frac{d}{dt}\underline{S} = \underline{\Omega} + \underline{\Omega}^\dagger \ , \tag{3.15}$$

the right-hand side of Eq. (3.14) is zero ensuring that the norm N of a MO does not depend on time.

Transforming the matrix of the kinetic energy operator $K \equiv = (\partial/\partial \mathbf{r})^2/2$ appearing in Eq. (3.6), by means of Eqs. (2.2) and (3.9), one can derive the following relationship:

$$\underline{K} = \tfrac{1}{2}(\underline{K}^{(N)} + [\underline{K}^{(N)}]^\dagger) - \underline{V}_\Omega \ , \tag{3.16}$$

where

$$K^{(N)}_{\mu\zeta,\mu'\zeta'} = -\tfrac{1}{2}\int d\mathbf{r}_1 \exp\{-i[\alpha_{n'}(\mathbf{r}_1) - \alpha_n(\mathbf{r}_1)]\} \times \chi_\mu(\mathbf{r}_{n1})^* \left[\frac{\partial}{\partial \mathbf{r}_{n'1}}\right]^2 \chi_{\mu'}(\mathbf{r}_{n'1})\delta_{\zeta\zeta'} \tag{3.17}$$

and

$$\underline{V}_\Omega = -\frac{i}{2}(\underline{\Omega} - \underline{\Omega}^\dagger) \ . \tag{3.18}$$

The matrix $\underline{K}^{(N)}$, defined by its elements in Eq. (3.17), is a transformed kinetic energy matrix obtained by shifting the origin of the electronic coordinates to the nuclear positions.

Making use of Eqs. (3.15) and (3.16), we obtain the new Fock matrix

$$\underline{F}^{(N)} = \underline{F} + \underline{V}_\Omega \tag{3.19}$$

and the TDHF equations in the TAO basis-set representation

$$i\frac{d}{dt}\underline{c}_j = \underline{S}^{-1}\left[\underline{F}^{(N)} + \underline{V}_L - i\frac{1}{2}\frac{d}{dt}\underline{S}\right]\underline{c}_j, \quad j = 1,2 \ . \tag{3.20}$$

The Fock matrix $\underline{F}^{(N)}$ depends on both $\underline{c}_1$ and $\underline{c}_2$, so Eq.

(3.20) represents a set of $2\times(M_a+M_b)$ coupled, complex, first-order, nonlinear differential equations for the coefficients c.

IV. THE MODEL

We shall consider collisions of the systems He + He^{2+}, and $\mathrm{He}^{+}(\uparrow)+\mathrm{He}^{+}(\downarrow)$, where the arrows indicate an electronic state with spins up or down.

In the collision energy range of $E=10-100$ keV, the ratio of the nuclear velocity to the characteristic electron velocity in the ground state of the He^{+} ion varies between 0.112 and 0.354. This indicates a need for translation factors in any realistic calculation that aims to compare with experimental results.

The goal of the present paper, however, is to compare results of different approximations within a reasonable realistic model where exact solutions are also feasible. Therefore, in order to simplify things, we shall consistently neglect the effects of the translation factors, i.e., we let $\alpha_n\rightarrow 0$, after having calculated the necessary matrix elements in Eq. (3.20). In what follows, matrices will represent operators in an ordinary atomic orbital (AO) basis.

As our model, we chose a minimal AO basis set with only one 1s Slater-type orbital $\chi_n(r_n)$ centered at each of the two nuclei $n=a,b$:

$$\chi_n=(\gamma_n^3/\pi)^{1/2}\exp(-\gamma_n r_n)\ ,$$

with exponents $\gamma_a=\gamma_b=2.0a_B^{-1}$, in atomic units, for helium.

A. Solutions of the TDHF equations

For computational purposes we have chosen to write Eq. (3.20) in a Hermitian form by applying the basis-set transformation

$$\underline{c}=\underline{S}^{1/2}\underline{C}\ . \tag{4.1}$$

We then obtain from Eq. (3.20) the following Hermitian matrix-differential equation for $\underline{C}(t)$:

$$i\frac{d}{dt}\underline{C}=\underline{S}^{-1/2}(\underline{F}^{(N)}+\underline{V}_L+\underline{V}_S)\underline{S}^{-1/2}\underline{C}\ , \tag{4.2}$$

where

$$\underline{V}_S=\frac{i}{2}\left[\underline{S}^{1/2},\frac{d}{dt}\underline{S}^{1/2}\right]\ . \tag{4.3}$$

The use of the 1s AO basis set greatly simplifies the structure of the TDHF equations (4.2).

First of all, only Σ states may occur with $M_L=0$, where M_L is the component of the total orbital angular momentum along the axis of quantization. It follows that in this case the Coriolis coupling $\underline{V}_L$ is identically zero, which can be seen by recalling that the operator L_y couples only those states for which $|\Delta M_L|=1$.

Secondly, the overlap matrix $\underline{S}$ has the very simple form

$$\underline{S}=\begin{bmatrix}1 & s\\ s & 1\end{bmatrix}\ , \tag{4.4a}$$

where

$$s(t)=\langle\chi_a(t)\,|\,\chi_b(t)\rangle\ . \tag{4.4b}$$

The matrices $\underline{S}^{-1/2}$, $\underline{S}^{1/2}$, and $d\underline{S}^{1/2}/dt$ are easy to calculate, and one finds that the commutator in Eq. (4.3) vanishes, i.e., that $\underline{V}_S\equiv 0$, in this model. Equation (4.2) then reduces to the following simple form:

$$i\frac{d}{dt}\underline{C}_j=\underline{S}^{-1/2}\underline{F}^{(N)}\underline{S}^{-1/2}\underline{C}_j,\quad j=1,2\ . \tag{4.5}$$

All the matrix elements of $\underline{S}^{-1/2}$ and $\underline{F}^{(N)}$ can be calculated analytically.[26]

Let us introduce the following notation: $\chi_n[r_{nj}(t_1)]\equiv\bar{\chi}_n(j)$, $n=a,b$, where t_1 is the initial time. At $t=t_1$ ($R\rightarrow\infty$) there are four linearly independent Hartree-Fock states, $D_i(t_1)$, $i=1,\ldots,4$, with $M_L=0$:

$$D_1(t_1)=\bar{\chi}_a(1)\bar{\chi}_a(2)\,{}^1\Theta(1,2)\ , \tag{4.6a}$$

$$D_2(t_1)=\bar{\chi}_b(1)\bar{\chi}_b(2)\,{}^1\Theta(1,2)\ , \tag{4.6b}$$

$$D_3(t_1)=(\tfrac{1}{2})^{1/2}[\bar{\chi}_a(1)\bar{\chi}_b(2)\alpha(1)\beta(2)-\bar{\chi}_b(1)\bar{\chi}_a(2)\beta(1)\alpha(2)]\ , \tag{4.6c}$$

$$D_4(t_1)=(\tfrac{1}{2})^{1/2}[\bar{\chi}_b(1)\bar{\chi}_a(2)\alpha(1)\beta(2)-\bar{\chi}_a(1)\bar{\chi}_b(2)\beta(1)\alpha(2)]\ , \tag{4.6d}$$

where ${}^1\Theta(1,2)$ is the two-electron singlet spin function constructed from the spin eigenfunctions α and β.

The antisymmetric two-electron functions $D_i(t_1)$, $i=1,\ldots,4$, form an orthonormal set, and correspond to the following initial channels, respectively, He + He^{2+}, He^{2+} + He, $\mathrm{He}^{+}(\uparrow)+\mathrm{He}^{+}(\downarrow)$, and $\mathrm{He}^{+}(\downarrow)+\mathrm{He}^{+}(\uparrow)$.

From Eqs. (3.2), (3.11), and (4.6) it follows that the TDHF equations (4.5) should be solved by setting $C_{jn}(t_1)$ equal to zero or one. For instance, the initial values $C_{1a}(t_1)=C_{2a}(t_1)=1$, and $C_{1b}(t_1)=C_{2b}(t_1)=0$ give the initial state specified in Eq. (4.6a). Note that at $t=t_1$, i.e., when $R\rightarrow\infty$, $\underline{S}$ becomes the unit matrix and, in accordance with Eq. (4.1), one has $\underline{C}(t_1)=\underline{c}(t_1)$; the same is valid at the final asymptotic time $t=t_2$.

B. The "exact" solution

From the two 1s AO's, $\chi_n[r_{nj}(t)]\equiv\chi_n(j)$, $n=a,b$, $j=1,2$, one can construct the following set of linearly independent, antisymmetric two-electron basis functions, $\Phi_i(\mathbf{x}_1,\mathbf{x}_2;t)$:

$$\Phi_1=N_+[\chi_a(1)\chi_a(2)+\chi_b(1)\chi_b(2)]\,{}^1\Theta(1,2)\ , \tag{4.7a}$$

$$\Phi_2=N_-[\chi_a(1)\chi_a(2)-\chi_b(1)\chi_b(2)]\,{}^1\Theta(1,2)\ , \tag{4.7b}$$

$$\Phi_3=N_+[\chi_a(1)\chi_b(2)+\chi_b(1)\chi_a(2)]\,{}^1\Theta(1,2)\ , \tag{4.7c}$$

$$\Phi_4=N_-[\chi_a(1)\chi_b(2)-\chi_b(1)\chi_a(2)]\,{}^3\Theta(1,2)\ , \tag{4.7d}$$

where

$$N_\pm=(1/\{2[1\pm s(t)^2]\})^{1/2}\ , \tag{4.8}$$

$${}^{1}\Theta(1,2)=(\tfrac{1}{2})^{1/2}[\alpha(1)\beta(2)-\beta(1)\alpha(2)]\ , \tag{4.9a}$$

$${}^{3}\Theta(1,2)=(\tfrac{1}{2})^{1/2}[\alpha(1)\beta(2)+\beta(1)\alpha(2)]\ , \tag{4.9b}$$

and $s(t)$ in Eq. (4.8) is given by Eq. (4.4b).

We define

$$\Phi^{(e)}(\mathbf{x}_1,\mathbf{x}_2;t)=\sum_{i=1}^{4} g_i(t)\Phi_i(\mathbf{x}_1,\mathbf{x}_2;t) \tag{4.10}$$

as the "exact" solution of the Schrödinger equation (2.9) within our minimal basis model, where $\underline{g}=[g_i]$ satisfies

$$i\frac{d}{dt}\underline{g}=\underline{\Gamma}^{-1}\left[\underline{H}^{(N)}-i\frac{1d}{2dt}\underline{\Gamma}\right]\underline{g}\ . \tag{4.11}$$

This equation was derived following the same procedure as in the TDHF case in Sec. III. First, we wrote the functions Φ_j in Eqs. (4.7) in terms of TAO's and calculated the necessary matrix elements. In this way we eliminated the spurious momentum-coupling term, and then took the limit $\alpha_n \rightarrow 0$ arriving at Eq. (4.11) where $\underline{H}^{(N)}$, similarly to $\underline{F}^{(N)}$ in Eq. (3.16), contains matrix elements of the one-electron kinetic energy operator in coordinates referred to the positions of the nuclei.

From Eqs. (4.7)–(4.9) it follows that

$$\begin{aligned}\Gamma_{ij}\equiv\langle\Phi_i\mid\Phi_j\rangle&=1, \quad \text{for } i=j\\ &=\gamma(t), \quad \text{for } i,j=1,3,\quad i\neq j\\ &=0, \quad \text{otherwise}\ ,\end{aligned} \tag{4.12a}$$

$$\gamma(t)=2s(t)/[1+s(t)^2]\ , \tag{4.12b}$$

and also that the only nonzero off-diagonal elements of $\underline{H}^{(N)}$ are $H_{13}^{(N)}=H_{31}^{(N)}$. The determinant of the overlap matrix is $\det(\underline{\Gamma})=1-\gamma^2(t)$. As one can see from Eqs. (4.12b) and (4.4b), $\underline{\Gamma}$ is singular in the united-atom limit ($R\rightarrow 0$).

From the structure of the matrices $\underline{\Gamma}$ and $\underline{H}^{(N)}$ it follows that only two of the coefficients (g_1 and g_3) are coupled, and that

$$g_2(t)=g_2(t_1)\exp\left[-i\int_{t_1}^{t}dt'H_{22}^{(N)}(t')\right]\ , \tag{4.13}$$

$$g_4(t)=g_4(t_1)\exp\left[-i\int_{t_1}^{t}dt'H_{44}^{(N)}(t')\right]\ . \tag{4.14}$$

Introducing the 2×2 matrices

$$\underline{\Gamma}'=\begin{bmatrix}1 & \gamma\\ \gamma & 1\end{bmatrix},\quad \underline{H}'=\begin{bmatrix}H_{11}^{(N)} & H_{13}^{(N)}\\ H_{31}^{(N)} & H_{33}^{(N)}\end{bmatrix}\ ,$$

and the two-dimensional column vector

$$\underline{g}'=\begin{bmatrix}g_1\\ g_3\end{bmatrix}\ ,$$

one obtains

$$i\frac{d}{dt}\underline{g}'=(\underline{\Gamma}')^{-1}\left[\underline{H}'-i\frac{1}{2}\frac{d}{dt}\underline{\Gamma}'\right]\underline{g}'\ , \tag{4.15a}$$

or, with $\underline{g}'=(\underline{\Gamma}')^{1/2}\underline{G}'$, and realizing that

$$\left[(\underline{\Gamma}')^{1/2},\frac{d}{dt}(\underline{\Gamma}')^{1/2}\right]=0\ ,$$

$$i\frac{d}{dt}\underline{G}'=(\underline{\Gamma}')^{-1/2}\underline{H}'(\underline{\Gamma}')^{-1/2}\underline{G}'\ . \tag{4.15b}$$

Equation (4.15b) can be easily transformed into the interaction picture

$$i\frac{d}{dt}\underline{G}_I'=\underline{H}_I'\underline{G}_I'\ , \tag{4.16a}$$

$$\underline{H}_I'=(\underline{U}_0')^{\dagger}[(\underline{\Gamma}')^{-1/2}\underline{H}'(\underline{\Gamma}')^{-1/2}-\underline{H}_0']\underline{U}_0'\ , \tag{4.16b}$$

$$\underline{U}_0'(t,0)=\exp\left[-i\int_0^t dt'\underline{H}_0'(t')\right]\ , \tag{4.16c}$$

$$\underline{H}_0'=\lim_{R\rightarrow\infty}\underline{H}'\ , \tag{4.16d}$$

and it can be solved by standard numerical techniques.

At the initial time $t=t_1$, the basis functions $\Phi_j(t)$, in Eqs. (4.7), can be expressed in terms of the HF initial states $D_i(t_1)$ of Eqs. (4.6):

$$\Phi_1(t_1)=(\tfrac{1}{2})^{1/2}[D_1(t_1)+D_2(t_1)]\ , \tag{4.17a}$$

$$\Phi_2(t_1)=(\tfrac{1}{2})^{1/2}[D_1(t_1)-D_2(t_1)]\ , \tag{4.17b}$$

$$\Phi_3(t_1)=(\tfrac{1}{2})^{1/2}[D_3(t_1)+D_4(t_1)]\ , \tag{4.17c}$$

$$\Phi_4(t_1)=(\tfrac{1}{2})^{1/2}[D_3(t_1)-D_4(t_1)]\ . \tag{4.17d}$$

We obtain the initial values $g_i(t_1)$ for a given initial state $D^{(+)}(t_1)$ by inverting Eqs. (4.17). For example, to calculate transitions from initial channel 1 (He + He^{2+}, in state D_1) to final channel 3 [He$^{+}(\uparrow)$+He$^{+}(\downarrow)$, in state D_3], one first solves Eq. (4.13) with $g_2(t_1)=(\frac{1}{2})^{1/2}$, Eq. (4.14) with $g_4(t_1)=0$ which gives $g_4(t_1)\equiv 0$, as well as Eq. (4.15b) with initial conditions $g_1(t_1)=G_1'(t_1)=(\frac{1}{2})^{1/2}$ and $g_3(t_1)=G_2'(t_1)=0$; then one calculates $\Phi^{(e)}$ from Eq. (4.10), and finally one projects $\Phi^{(e)}(t_2)$ onto $D_3(t_2)$ which is similar to $D_3(t_1)$ defined by Eq. (4.6c).

V. NUMERICAL PROCEDURE AND RESULTS

Our goal is to calculate the transition amplitudes $\mathcal{S}_{fi}$ as defined by Eqs. (2.13) and (2.14), using the TDHF solutions as approximate wave functions, i.e., $\Phi^{(\pm)}=D^{(\pm)}$. In order to do this, we need to solve the TDHF equations (4.5) twice, first by integrating forward from the time t_1 with given initial conditions $D^{(+)}(t_1)$, then by calculating a solution by backward integration from t_2 with a different starting condition $D^{(-)}(t_2)$.

Equation (4.5) represents four coupled differential equations for the AO coefficients, which are easy to separate into eight real equations for the real and imaginary parts of the unknown linear combination coefficients $C_{nj}^{(\pm)}$, $n=a,b$, $j=1,2$. The numerical integrations have been performed by using the algorithm *DE*, an Adam-Peace predictor-corrector method.[27] This procedure has the advantage that it automatically adjusts the stepsize of the integration in accordance with the accuracy required. The integrals of the phases $\Delta^{(\pm)}$ in Eqs. (2.14) can be generated along with the solutions $D^{(\pm)}$, and their computation requires the same one- and two-center integrals as those

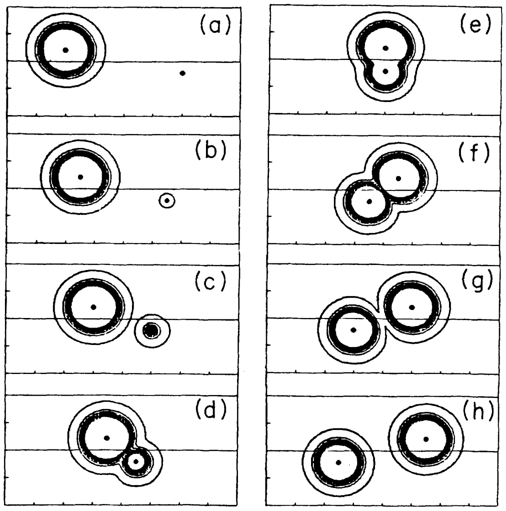

FIG. 2. Time evolution of the 1s electronic isodensity curves obtained from the TDHF solutions for the one-electron-transfer process in the collision of He and He^{2+}. The initial and the final separation of the two nuclei along the z direction is $8.0a_B$, and the collision energy is 50 keV.

needed in $D^{(\pm)}$.

Since we needed an additional time integral to calculate the expressions in Eqs. (2.14), solving for $D^{(+)}$ and $D^{(-)}$ separately proved to be unpractical. Therefore we first integrated Eq. (4.5) backward in time from t_2 and obtained $D^{(-)}$ at the time t_1. Using the computed coefficients $C_{nj}^{(-)}(t_1)$, together with the already specified $C_{nj}^{(+)}(t_1)$'s as initial values, we solved for $\underline{C}_j^{(+)}(t)$ and $\underline{C}_j^{(-)}(t)$ simultaneously, and at the same time generated the required integrals over time in Eqs. (2.14). Although in this way we solved Eq. (4.5) three times, the effective computing time was reduced by a factor of about 5, because no interpolation between separately stored solutions $D^{(+)}$ and $D^{(-)}$ was needed.

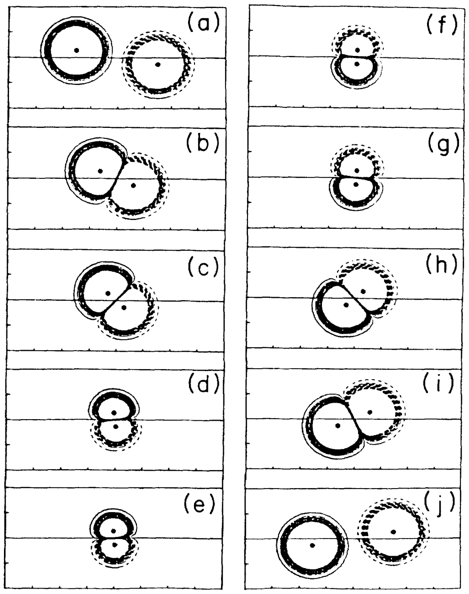

FIG. 3. Time evolution of the spin densities obtained from the TDHF wave functions for the spin-flip process $He^+(\uparrow)+He^+(\downarrow)\rightarrow He(\downarrow)+He(\uparrow)$. The initial separation between the two nuclei is $6.0a_B$, and the collision energy is 50 keV.

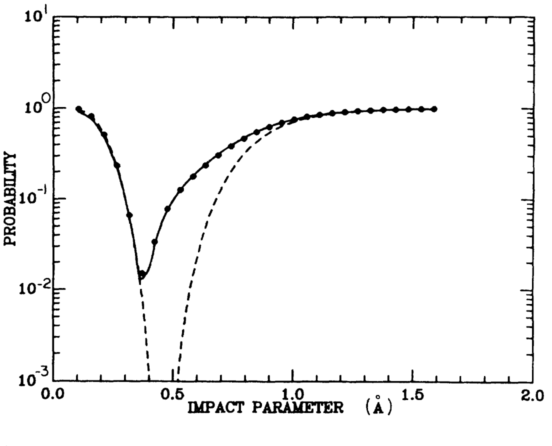

FIG. 4. Transition probabilities vs impact parameters for the elastic scattering of He and He^{2+}, at $E=100$ keV. Solid line, exact results; dashed line, results obtained from the TDHF solutions by forward integration; dots, results obtained by the variational-functional method.

In the case of the exact solutions, we solved Eqs. (4.16) for the coefficients g_1 and g_3 with the algorithm *DE* mentioned previously; the integrals in Eqs. (4.13) and (4.14) for g_2 and g_4, respectively, were computed while generating the coefficients g_1 and g_3. The initial conditions for the g's were chosen according to Eq. (4.17).

The time development of the one-electron densities gives a clear picture of the electronic rearrangement processes. This is demonstrated in Figs. 2 and 3. In Fig. 2,

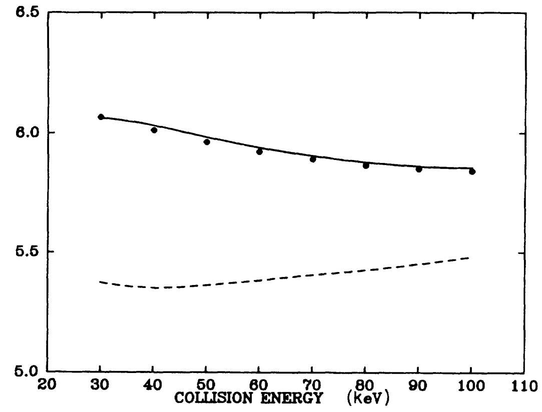

FIG. 5. Elastic cross sections vs collision energies for collision of He and He^{2+}. Solid line, exact results; dashed line, results obtained from the TDHF solutions by forward integration; dots, results obtained by the variational-functional method.

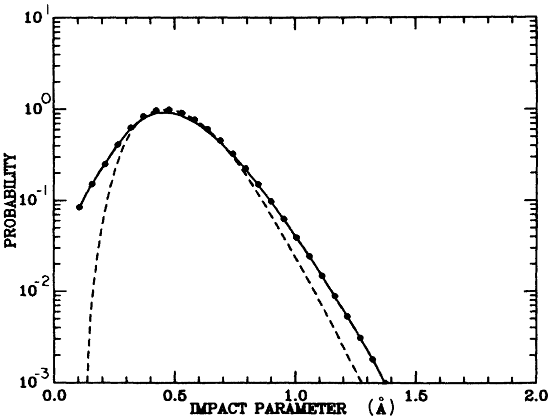

FIG. 6. One-electron-transfer transition probabilities vs impact parameters for the collision of He and He^{2+}, at $E=100$ keV.

the time evolution of the one-electron densities is shown for the one-electron transfer collision process He $+ He^{2+} \rightarrow He^+ + He^+$. Here we have summed over the final spin states. We started (a) and ended (h) the collision when the separation between the two nuclei along the z direction was larger than $8.0a_B$, in atomic units. In this case the relative collision energy was 50 keV, and the impact parameter was $1.7a_B$. The isodensity curves correspond to values between 10^{-4} and 10^{-2}. One sees that the electronic charge density is smoothly transferred from one nucleus to the other.

In Fig. 3 we show the spin-flip collision process $He^+(\uparrow)+He^+(\downarrow)\rightarrow He^+(\downarrow)+He^+(\uparrow)$. The dashed isodensity curves correspond to negative, or spin-down, values. The collision time increases from (a) to (j). Here the maximum separation between the nuclei along the z direction was $6.0a_B$, and the energy was 50 keV. The spin density is seen to smoothly shrink until the nuclei come to their closest approach, around which the spin densities abruptly reverse sign.

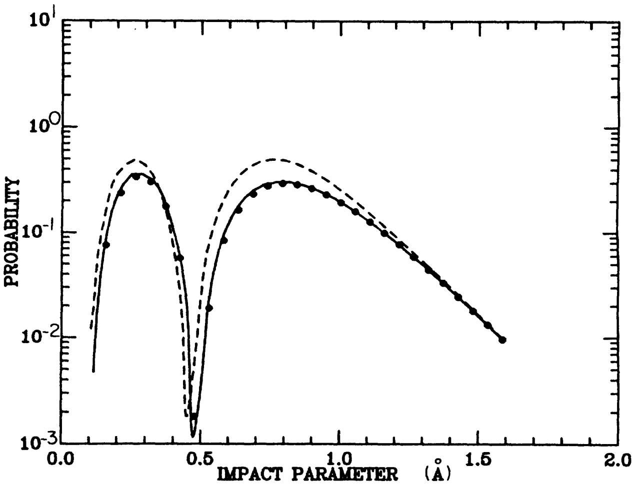

FIG. 8. Two-electron-transfer transition probabilities vs impact parameters for the collision of He and He^{2+}, at $E=100$ keV.

Transition probabilities as functions of the impact parameter in the range of $0.2a_B$–$3.0a_B$, and cross sections versus collision energies in the range of 30–100 keV were calculated with the exact solutions, with the TDHF(+) ones, as well as with the functional method, for the following processes:

$$He+He^{2+}\rightarrow He+He^{2+} , \tag{5.1}$$

$$He+He^{2+}\rightarrow He^{2+}+He , \tag{5.2}$$

$$He+He^{2+}\rightarrow He^{+}+He^{+} , \tag{5.3}$$

$$He^+(\uparrow)+He^+(\downarrow)\rightarrow He^+(\uparrow)+He^+(\downarrow) , \tag{5.4}$$

$$He^+(\uparrow)+He^+(\downarrow)\rightarrow He^+(\downarrow)+He^+(\uparrow) . \tag{5.5}$$

The state-to-state cross section σ_{fi} for scattering within $0\leq\theta\leq\theta_0$ is defined as

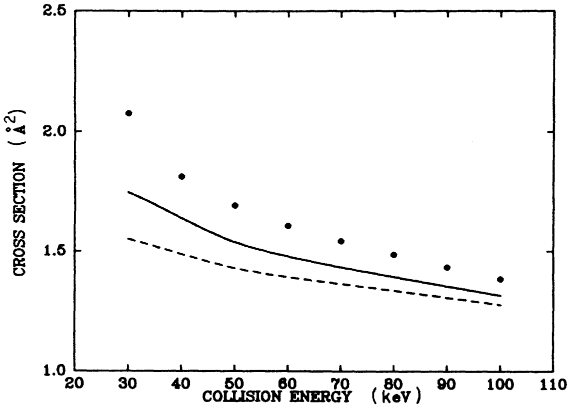

FIG. 7. One-electron-transfer cross sections vs collision energies for the collision of He and He^{2+}.

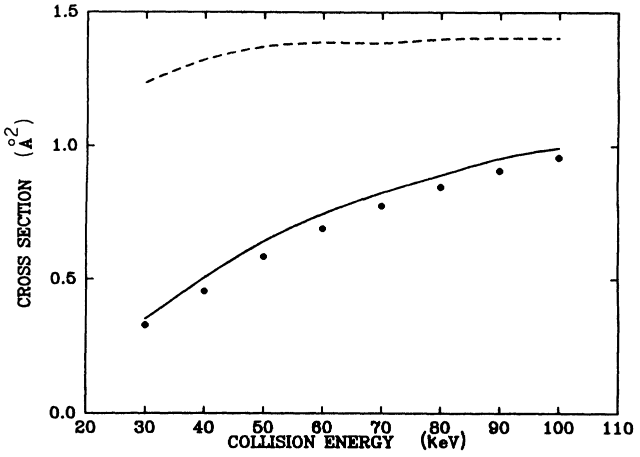

FIG. 9. Two-electron-transfer cross sections vs collision energies for the collision of He and He^{2+}.

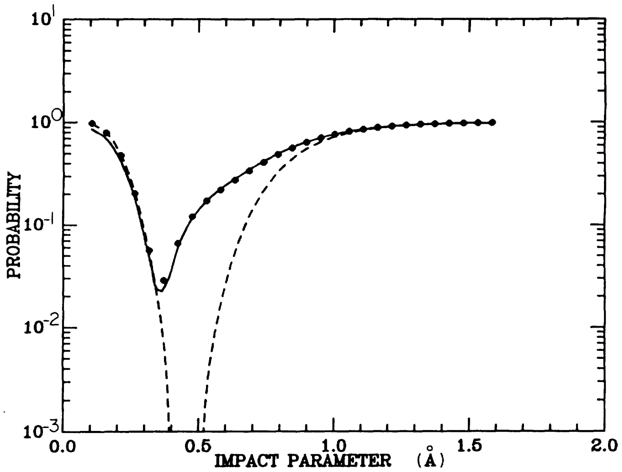

FIG. 10. Transition probabilities vs impact parameters for the elastic process $\mathrm{He}^+(\uparrow)+\mathrm{He}^+(\downarrow)\rightarrow\mathrm{He}^+(\uparrow)+\mathrm{He}^+(\downarrow)$ at $E=100$ keV.

$$\sigma_{fi}=2\pi\int_{b_0}^{\infty} bP_{fi}(b)db \ , \tag{5.6}$$

where

$$b_0=\left|\,2/[E\tan(\theta_0/2)]\,\right|$$

is the impact parameter corresponding to the deflection angle θ_0 for the classical Coulomb scattering of α particles determined by the opening of the detector. In our calculations we have chosen $\theta_0=1°$.

The Hartree-Fock probabilities $P_{fi}^{(+)}$ and $P_{fi}^{(-)}$ (and the corresponding cross sections) are equal due to symmetry for all collision processes except that in Eq. (5.3). However, even in this case the two functions $P_{fi}^{(+)}(b)$ and $P_{fi}^{(-)}(b)$ [and also $\sigma_{fi}^{(+)}(E)$ and $\sigma_{fi}^{(-)}(E)$] coincided within the linewidth of the curves, in the present study. Results for the processes of Eqs. (5.1)–(5.5) are shown in Figs. 4–13. We plotted the probabilities versus the impact parameters only at $E=100$ keV.

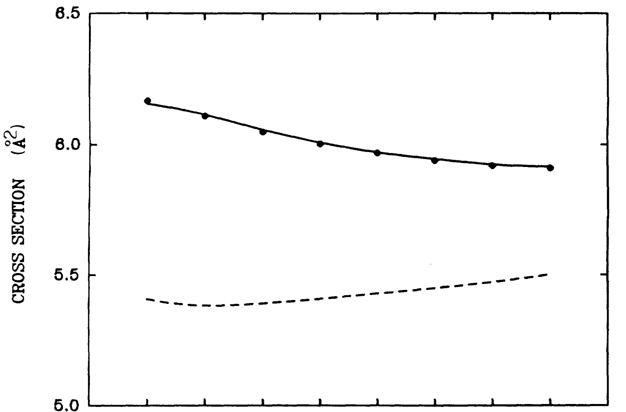

FIG. 11. Elastic cross sections vs collision energies for the process $\mathrm{He}^+(\uparrow)+\mathrm{He}^+(\downarrow)\rightarrow\mathrm{He}^+(\uparrow)+\mathrm{He}^+(\downarrow)$.

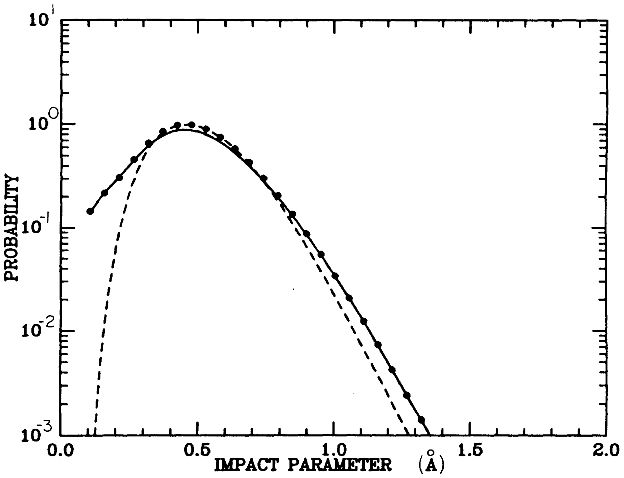

FIG. 12. Transition probabilities vs impact parameters for the spin-flip (two-electron-transfer) process $\mathrm{He}^+(\uparrow)+\mathrm{He}^+(\downarrow)\rightarrow\mathrm{He}^+(\downarrow)+\mathrm{He}^+(\uparrow)$ at $E=100$ keV.

VI. CONCLUSIONS

As we can see from the results shown in Figs. 4–13, remarkable improvements over the standard TDHF results can be achieved by using the phase-independent transition-amplitude functional of Eqs. (2.13) and (2.14). This involves the calculation of two Slater determinants $D^{(+)}(t)$ and $D^{(-)}(t)$ and the computation of three numerical quadratures over the time variable. But compensating for this additional work, the present method does not require any molecular integrals other than those generated to construct the Fock matrix.

The difference between the cross sections obtained by the three different methods is, on the average, within 20%, except in the case of the one-electron transfer process $\mathrm{He}+\mathrm{He}^{2+}\rightarrow\mathrm{He}^{+}+\mathrm{He}^{+}$, where the results of the standard TDHF method are about 100% larger than those of the exact one. Note that the vertical scales in Figs. 5, 7, 11, and 13 do not begin at zero Å^2.

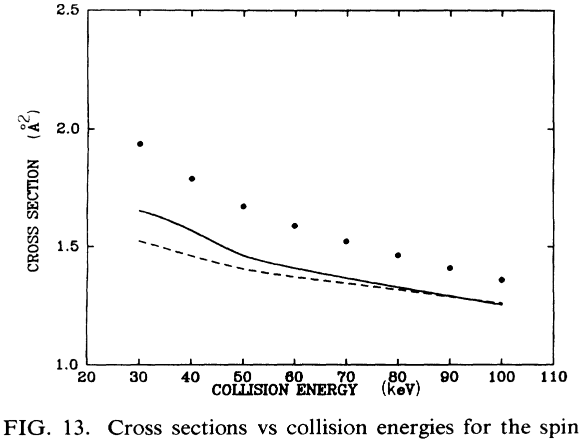

FIG. 13. Cross sections vs collision energies for the spin-flip (two-electron-transfer) process $\mathrm{He}^+(\uparrow)+\mathrm{He}^+(\downarrow)\rightarrow\mathrm{He}^+(\downarrow)+\mathrm{He}^+(\uparrow)$.

In the case of the two-electron transfer [Eq. (5.2)] and the spin-flip [Eq. (5.5)] processes, the standard TDHF cross sections seem to be as accurate as the ones calculated by the functional method (see Figs. 7 and 13). However, from Figs. 6 and 12 it is obvious that this is due to a systematic cancellation of errors, since the standard TDHF results overestimate the probabilities at the maxima, and underestimate them in the large impact-parameter domain, as compared to the exact ones.

We have also performed calculations by using the Demkov functional[17] of Eq. (2.15), and have indeed found that the denominator in the complex phase

$$\langle D^{(-)}|[H-i(\partial/\partial t)]D^{(+)}\rangle/\langle D^{(-)}|D^{(+)}\rangle$$

can, in certain cases, cause serious errors. This is demonstrated in Fig. 14, where we have also plotted the probabilities obtained from Eq. (2.15) (open circles) in the case of the spin-flip process at $E=50$ keV. Here one can see that besides an obvious singularity observed between $b=0.2$ and 0.3 Å, expression (2.15) yields poorer results than our functional method does.

Numerical calculations with the variational functional of Eqs. (2.13) and (2.14) without the phases $\Delta^{(\pm)}$ [i.e., setting $\Delta^{(\pm)}=0$, everywhere in Eqs. (2.14)] gave results far from the correct ones. Hence, in addition to the formal advantage of having a phase-independent variational expression. We conclude that the introduction of the real phases $\Delta^{(\pm)}(t)$ in the transition amplitude is essential to obtain meaningful results.

Finally, it should be emphasized that our computational method can be extended to cases requiring larger basis sets of traveling atomic orbitals. Such an extension would allow us to calculate transition probabilities for conditions of experimental interest, and is presently being undertaken. In the present contribution we have chosen to work with a small basis set, which allowed us to solve for the exact transition probabilities, to determine by comparison the quality of the results we obtained from our variational functional.

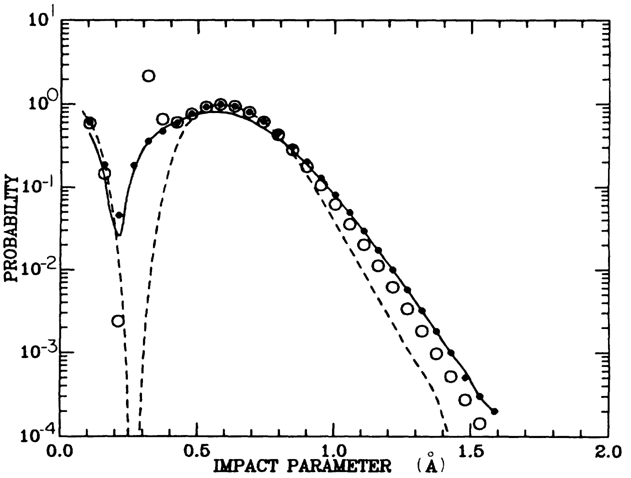

FIG. 14. Transition probabilities vs impact parameters for the spin-flip (two-electron-transfer) process $\mathrm{He}^+(\uparrow)+\mathrm{He}^+(\downarrow)\rightarrow\mathrm{He}^+(\downarrow)+\mathrm{He}^+(\uparrow)$ at $E=50$ keV. The open circles show results obtained from the Demkov functional of Eq. (2.15).

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