

Offsetting the difficulties of the molecular model of atomic collisions in the intermediate velocity range

L. F. Errea, L. Méndez, and A. Riera

Departamento de Química, C-XIV, Universidad Autónoma de Madrid, Canto Blanco, 28049 Madrid, Spain

(Received 5 June 1989; revised manuscript received 29 November 1990)

To offset the defective behavior of the molecular method of atomic collisions at intermediate energies, we propose a method to approximate the probability flux towards continuum and discrete states not included in the molecular basis. We check the degree of accuracy and limitations of the method for a model case where transition probabilities can be calculated exactly. An application to the benchmark case of $\text{He}^+ + \text{H}^+$ collisions is also presented, and yields complementary information on the properties of this approach.

I. INTRODUCTION

Generalization of the molecular method of atomic collisions with the inclusion of translation factors¹⁻⁶ permits one to treat charge-exchange processes up to the energy region where their cross section is maximal. To determine these factors, in previous works⁷⁻¹² we minimized norms that measure couplings with states that are neglected in the molecular expansion, and our conclusions⁸⁻¹² have been widely used for systems with one¹³ and two¹⁴ active electrons. On the other hand, at higher collision energies such that electronic and nuclear velocities are comparable, this approach often fails¹³⁻¹⁵ to reproduce the rapid fall of charge-exchange cross sections beyond their maximum. Also, the large Euclidean and weighted norms indicate that ionization channels must be taken into account if one wishes to preserve a molecular description of the collision process. In the present work we propose a way to do so. A preliminary description of our approach in the general context of discrete-continuum transitions has been presented elsewhere.¹⁶

The introduction of ionization channels in a close-coupling expansion has been the object of several works,¹⁷⁻¹⁹ and in particular of recent articles of Thorson and Bandarage¹⁸ and Lüdde *et al.*²⁰⁻²² The former authors represented the molecular electronic continuum by packet states explicitly constructed from exact continuum ones. This yields an elegant and rigorous, though computationally involved,¹⁹ theory to calculate excitation, charge-exchange, and ionization cross sections. The approach of Lüdde, Ast, and Dreizler²⁰ is simpler, and has been applied in the framework of one-center²¹ and two-center²² atomic expansions. These authors account for the interaction between the states included in a close-coupling expansion and those left out through Feshbach-type²³ optical potentials; then local approximations are developed for the potential matrix elements.

In Sec. II we develop the ideas of the norm method⁷ so as to approximate the probability flux toward (continuum and discrete) states not included in the molecular basis. Illustrations for a model Hamiltonian such that the exact time evolution is known and for the benchmark case of $\text{He}^+ + \text{H}^+$ collisions provide complementary information on the performance of our method, and are presented in

Secs. III and IV, respectively. Atomic units are used unless otherwise stated.

II. THEORY

In the framework of the impact parameter semiclassical model, we start from a molecular ansatz for the electronic wave function:

$$\Phi = \sum_{k=1}^K a_k \varphi_k \exp \left[-i \int_0^t E_k dt' \right]. \quad (1)$$

We define⁷ the projectors P onto the manifold spanned by the wave functions included in (1), and Q onto its complement:

$$P = \sum_{k=1}^K |\varphi_k\rangle \langle \varphi_k|, \quad Q = 1 - P. \quad (2)$$

In the close-coupling approach Eq. (1) is substituted in the equation

$$iP \frac{\partial}{\partial t} P\Phi = PHP\Phi, \quad (3)$$

and the ensuing system of differential equations for the expansion coefficients is solved for each nuclear trajectory. We can compare Eq. (3) with the exact equation,

$$i \frac{\partial}{\partial t} \Psi = H\Psi, \quad (4)$$

or

$$iP \frac{\partial}{\partial t} P\Psi = PHP\Psi + P \left[H - i \frac{\partial}{\partial t} \right] Q\Psi, \quad (5a)$$

$$iQ \frac{\partial}{\partial t} Q\Psi = QHQ\Psi + Q \left[H - i \frac{\partial}{\partial t} \right] P\Psi. \quad (5b)$$

The last term in (5b) yields a probability leakage from P to Q space, which is not contemplated in (3). In turn, the resulting Q population influences that of the P functions through the last term in (5a). The operator $Q(H - id/dt)P$ is responsible for $P \rightarrow Q$ flux, i.e., it takes the state vector out of P space if initially it belonged to it. In our previous work⁷⁻¹⁰ we proposed to multiply the

molecular wave functions by translation factors chosen so as to minimize a measure of the P - Q coupling operator. One such measure, which gauges the overall quality of the P manifold, is provided by the Euclidean norm of the couplings between P and Q functions:

$$N = \left| \sum_{k=1}^K \left| \left| Q \left[H - i \frac{\partial}{\partial t} \right] P \varphi_k \right| \right|^2 \right|^{1/2}, \quad (6)$$

although in practice a more collision-specific criterion is often preferable, and this is given by the weighted norm

$$\begin{aligned} N_w &= \left| \sum_{k=1}^K |a_k|^2 \left| \left| Q \left[H - i \frac{\partial}{\partial t} \right] P \varphi_k \right| \right|^2 \right|^{1/2} \\ &= \left| \sum_{k=1}^K |a_k|^2 N_k^2 \right|^{1/2}, \end{aligned} \quad (7)$$

which also defines the partial norm N_k for the k th molecular state. It can be shown^{7,8} that $N_w \geq 0$ provides an upper bound and an oscillation-averaged measure for the deviation vector²⁴ between exact and approximate wave functions:

$$\varepsilon = \Psi - \Phi. \quad (8)$$

When the nuclear velocity v is comparable to those of the active electrons, one finds that N and N_w are large, which indicates that the $P \rightarrow Q$ probability flux cannot be neglected. However, when the P manifold is adequately chosen, it is reasonable to assume that we can approximate that missing flux through transitions to a small number of "probability absorbers" belonging to Q space. More specifically, we ascribe to any given P function φ_k an absorber state $\varphi_k^{(1)}$, such that, when added to the ansatz (1), the new partial norm N'_k is identically null along all nuclear trajectories, that is, such that $\varphi_k^{(1)}$ absorbs all direct probability leakage from φ_k toward Q space. We notice that it is impossible, in general, to achieve $N'_k \equiv 0$ by multiplying φ_k by a translation factor. Addition of these absorber states to the close-coupling basis may then be considered as a "best augmentation" procedure that selects, from Q space, those (nonadiabatic) functions that are more closely coupled to the P -space ones.

To infer the form of $\varphi_k^{(1)}$ let us assume that at $t = t_0$ the system is exactly described by φ_k . At $t = t_0 + \delta t$, the exact electronic wave function has evolved according to Eq. (4), while the approximation (1) fulfills Eq. (3), and it can be seen that the deviation vector is

$$\varepsilon(t) = -i(\delta t) Q \left[H - i \frac{\partial}{\partial t} \right] P \varphi_k(t) + (\delta t)^2. \quad (9)$$

Hence, when transitions from φ_k to Q space just begin to be important, the first term in (9) will be responsible for them. We now show that this Q function

$$\varphi_k^{(1)} = \frac{Q \left[H - i \frac{\partial}{\partial t} \right] P \varphi_k}{\left| \left| Q \left[H - i \frac{\partial}{\partial t} \right] P \varphi_k \right| \right|} \quad (10)$$

is the probability absorber sought. From Eq. (10) we have

$$N_k = \left\langle \varphi_k \left| H - i \frac{\partial}{\partial t} \right| \varphi_k^{(1)} \right\rangle. \quad (11)$$

Addition of $\varphi_k^{(1)}$ to P space yields a new projector,

$$Q' = Q - |\varphi_k^{(1)}\rangle\langle\varphi_k^{(1)}|, \quad (12)$$

fulfilling, from Eqs. (2) and (10),

$$Q' \left[H - i \frac{\partial}{\partial t} \right] \varphi_k = 0. \quad (13)$$

Hence, the new partial norm is $N'_k \equiv 0$ for all trajectories, as required.

Our proposal consists, therefore, in augmenting the molecular close-coupling basis by a (selected) set of absorbers. By taking these Q -space representatives as those functions that absorb all direct flux from P space one seeks to improve the convergence properties of the molecular expansion, and in particular to take into account the probability flux towards the ionization continua. This is obviously much simpler than augmenting the basis with continuum functions, but the price one pays for this simplicity is that, since absorbers are superpositions of discrete and continuum wave functions, the interpretation of their populations, e.g., as ionization probabilities, is not straightforward, and requires empirical verification.

At this stage of our development, it may be of interest to show that, from the formal point of view, the method can be made, in principle, as exact as required with regards to transition probabilities corresponding to P functions. For this, we generalize the idea of probability absorbers. For any given P function φ_k we define a sequence $\{\varphi_k^{(n)}; n=0, 1, \dots\}$ starting from $\varphi_k^{(0)} \equiv \varphi_k$, $Q_k^{(1)} = Q$:

$$\varphi_k^{(n)} = (N_k^{(n)})^{-1} Q_k^{(n)} \left[H - i \frac{\partial}{\partial t} \right] \varphi_k^{(n-1)}, \quad (14)$$

with

$$Q_k^{(n)} = Q_k^{(n-1)} - |\varphi_k^{(n-1)}\rangle\langle\varphi_k^{(n-1)}| \quad (15)$$

and

$$N_k^{(n)} = \left| \left| Q_k^{(n)} \left[H - i \frac{\partial}{\partial t} \right] \varphi_k^{(n-1)} \right| \right|. \quad (16)$$

It can then be easily seen that, for $n > 1$,

$$N_k^{(n)} = \left\langle \varphi_k^{(n-1)} \left| H - i \frac{\partial}{\partial t} \right| \varphi_k^{(n)} \right\rangle \quad (17)$$

and

$$\left\langle \varphi_k^{(n-1)} \left| H - i \frac{\partial}{\partial t} \right| \chi \right\rangle = 0 \quad (18)$$

if

$$\langle \varphi_k^{(n-2)} | \chi \rangle = \langle \varphi_k^{(n-1)} | \chi \rangle = \langle \varphi_k^{(n)} | \chi \rangle = 0 \quad (19)$$

and $\chi \equiv Q\chi$. We thus obtain an extension of Eqs. (11) and (13), whereby each member of the $\varphi_k^{(n)}$ sequence is an absorber for the previous one, $\varphi_k^{(n-1)}$; this latter function is only directly coupled to the former and (when $n > 1$) to $\varphi_k^{(n-2)}$; and there exist no couplings to functions orthogonal to the set $\{\varphi_k^{(n)}; k=0,1,\dots,K; n=0,1,\dots\}$. If at $t=t_0$ the state vector can be represented by a linear combination of φ_k ($k=1,\dots,K$), for $t \neq t_0$ it will stay immersed in the space spanned by $\{\varphi_k^{(n)}; k=1,\dots,K; n=0,1,2,\dots\}$. It may be remarked that, just as for atomic-orbital (AO), incremented AO (AO+), or triple-center expansions, this basis is probably formally overcomplete. This often results in a faster convergence, but we do not belabor this point since in actual calculations we shall keep to small values of n in $\varphi_k^{(n)}$, and for the present aim it is more practical to introduce a different generalization in the theory.

The generalization stems from the fact that, to fulfill the correct boundary conditions of the problem, translation factors are commonly introduced in the molecular functions. To be definite, suppose we choose a basis set $\{\varphi_k\}$ of adiabatic wave functions multiplied by a common translation factor²⁵ (CTF). Then the numerator in Eq. (10) can be written as a sum of radial $\varphi_k^{(R)}$ (proportional to v_z), rotational $\varphi_k^{(\theta)}$ (proportional to v_x), and $O(v^2)$ components, which unlike $\varphi_k^{(1)}$, transform like irreducible representations of the $C_{\infty v}$ point group and have couplings that are easily interpolated. In collisional problems it is then useful to separately incorporate these components as new terms in the basis.

Finally, it is often convenient to orthogonalize the resulting set of Q functions. For this purpose, although P -state populations are independent of the particular method employed, to be able to give a physical interpretation of the wave functions (as far as this is possible, as mentioned above), we have chosen the Wannier²⁶-Löwdin²⁷ orthogonalization procedure, which ensures a maximum preservation of character.

III. MODEL CALCULATION

We now illustrate for a model case such that the transition probabilities as functions of time and trajectory can be exactly evaluated, the accuracy and limitations of our method to deal with a competition between bound-bound and bound-continuum processes. The detailed information thus obtained cannot be reached from benchmark collisional calculations, for which exact time evolution is not available, nor from the example of Ref. 16.

We have chosen as model P space a two-dimensional manifold $\{\varphi_1, \varphi_2\}$. Q states are assumed to belong to the continuum spectrum, and to be coupled to φ_1 . To achieve physically meaningful P - Q couplings we have differentiated a fit of the sum of moduli of the radial couplings (modified by the CTF of Ref. 28) $S_1(E_j)$ between the HeH^{2+} $2p\sigma$ orbital and the pseudostates of positive energy E_j ($j=1,2,\dots,J$) obtained in the calculations of Refs. 8–10. For $R=2.3$ a.u. we compare in Fig. 1 the accumulated function $S_1(E_j)$ and its smoothed version. The values of $iv_z^{-1}\langle\varphi_1|-i\partial/\partial t|\varphi_E\rangle$ are displayed in Fig. 2, as a function of both E and R . The adiabatic energies

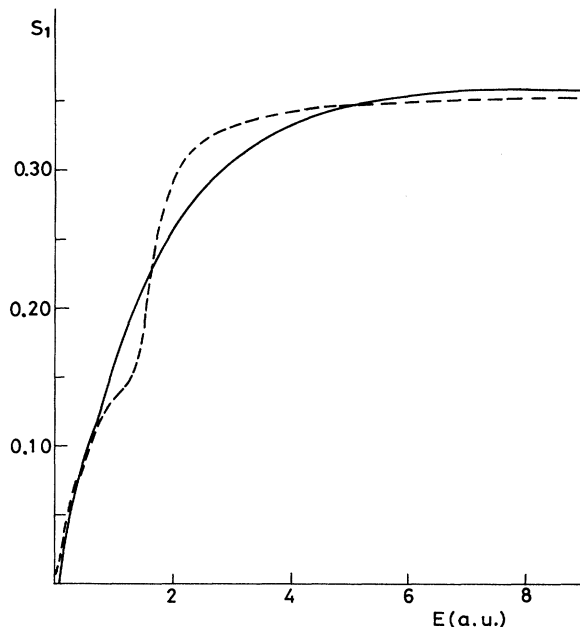


FIG. 1. (---), sum S_1 of the moduli of the modified radial coupling between the $2p\sigma$ orbital of HeH^{2+} and the pseudostates of positive energy calculated in Ref. 8, as a function of this energy, and for an internuclear distance $R=2.3$ a.u. (—), smoothing of this S_1 function.

$E_{1,2}$ [Fig. 3(a)] and the P - P dynamical coupling [Fig. 3(b)] were chosen so as to obtain sizable one-way transition probabilities for $v \approx 1$ a.u. The energies and couplings corresponding to $\varphi_1^{(1)}$ ($\equiv \varphi_1^{(R)}$ for the present illustration), calculated from exact sum-over-states expressions, are included in Fig. 3(a); for the sake of conciseness their analytical form is not given; it is available from the authors upon request.

We present in Figs. 4(a) ($v=1$), 4(b) ($v=1.5$), 4(c) ($v=2$), and 4(d) ($v=3$) exact and approximate transition probabilities $P_2 = |a_2(\infty)|^2$ times the impact parameter b ,

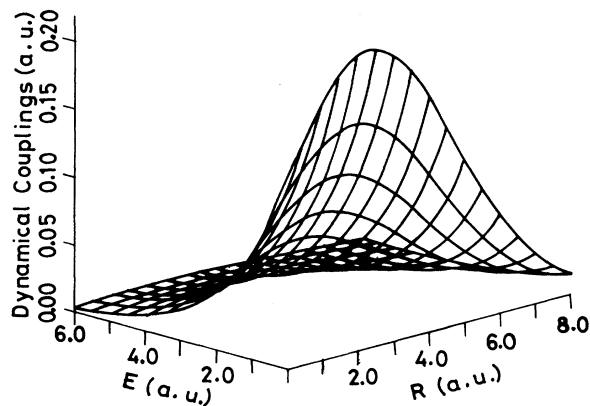


FIG. 2. Model dynamical coupling $iv_z^{-1}\langle\varphi_1|H-i\partial/\partial t|\varphi_E\rangle$ as a function of both energy E and internuclear distance calculated by differentiation of S_1 of Fig. 1.

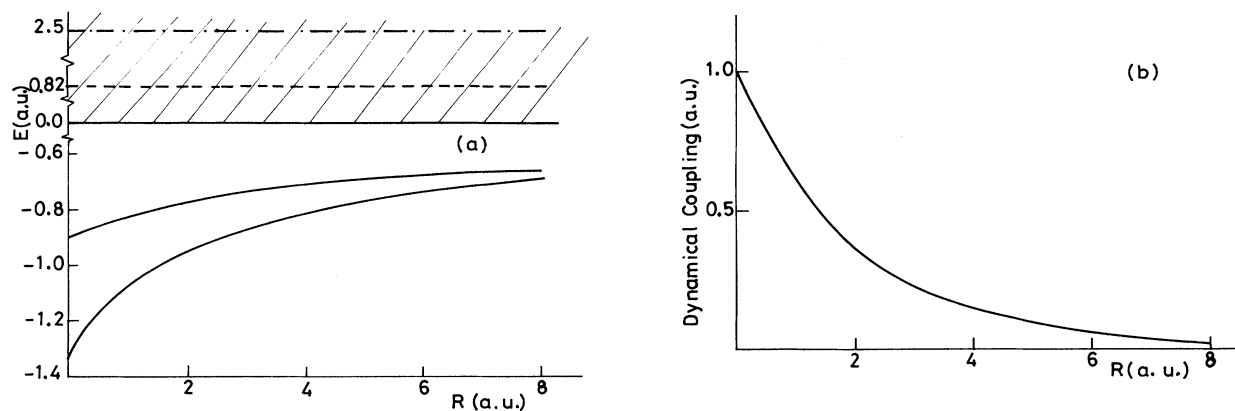


FIG. 3. (a) Model energies as functions of the internuclear distance R for —, the two adiabatic wave functions φ_1, φ_2 ; ---, the function $\varphi_1^{(1)}$; - · - · -, the function $\varphi_1^{(2)}$. (b) Dynamical coupling $iv_z^{-1} \langle \varphi_1 | H - i\partial/\partial t | \varphi_2 \rangle$.

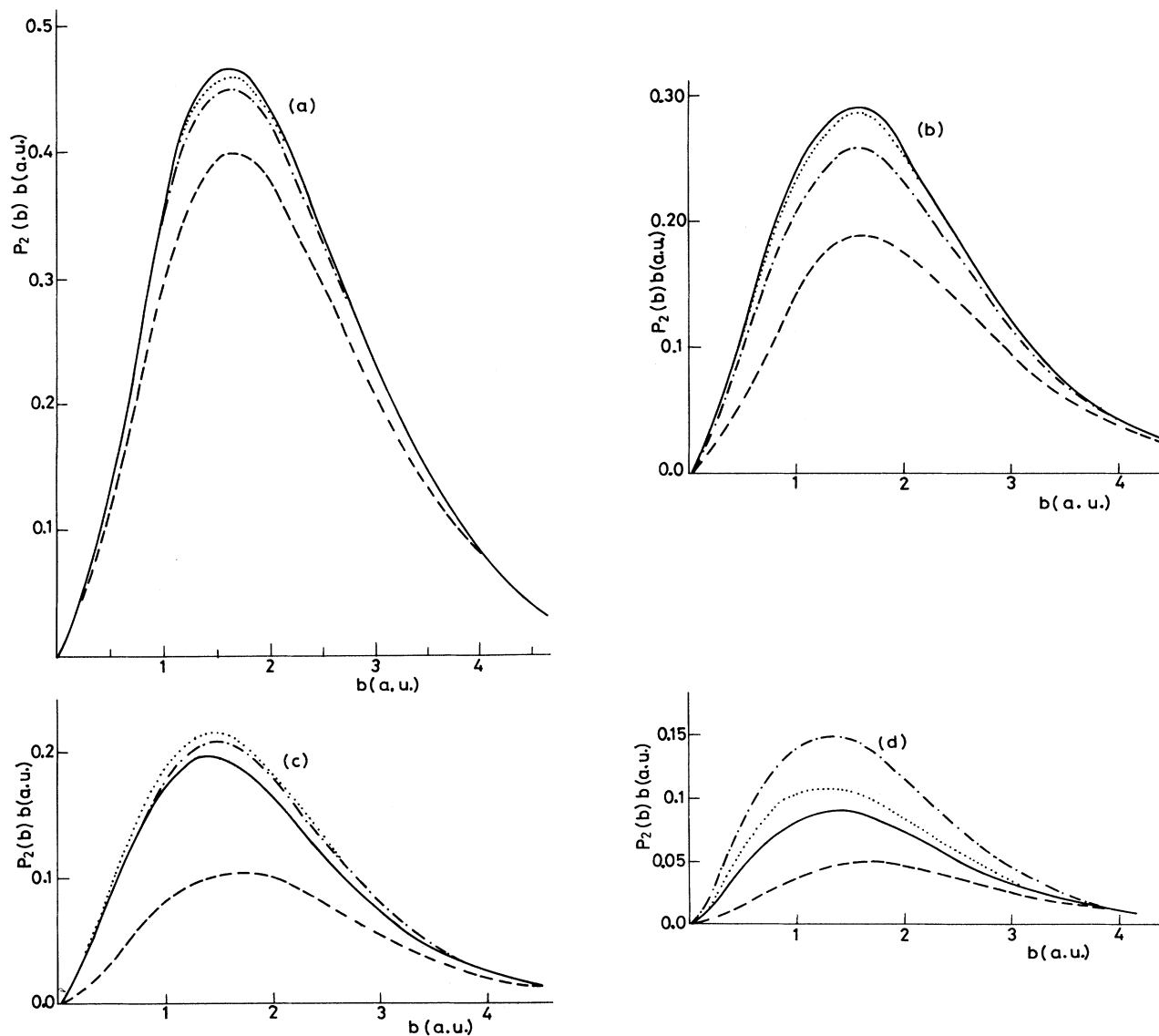


FIG. 4. "Charge-exchange" transition probability P_2 times the impact parameter b as a function of b for different values of the impact velocity: (a) $v=1.0$ a.u.; (b) $v=1.5$ a.u.; (c) $v=2.0$ a.u.; (d) $v=3.0$ a.u. —, exact result obtained by solution of Eq. (20); ---, two-state $\{\varphi_1, \varphi_2\}$ result; - · - · -, three-state $\{\varphi_1, \varphi_2, \varphi_1^{(1)}\}$ result; · · · ·, four-state $\{\varphi_1, \varphi_2, \varphi_1^{(1)}, \varphi_1^{(2)}\}$ result.

versus b . The corresponding “charge-exchange” cross sections are given in Fig. 5, together with the exact and approximate “ionization” cross sections. For the approximate calculations, we employed the program PAMPA²⁹ to integrate, along each nuclear trajectory $\mathbf{R}=\mathbf{b}+\mathbf{v}t$, the systems of differential equations that result when solving the impact-parameter equation in the representations $\{\varphi_1, \varphi_2\}$, $\{\varphi_1, \varphi_2, \varphi_1^{(1)}\}$, and $\{\varphi_1, \varphi_2, \varphi_1^{(1)}, \varphi_1^{(2)}\}$. For the exact calculations, we solved the set of integrodifferential equations:

$$i \frac{da_1}{dt} = a_2 \left\langle \varphi_1 \left| -i \frac{\partial}{\partial t} \right| \varphi_2 \right\rangle \exp \left[-i \int_0^t (E_2 - E_1) dt' \right] + \int dE a_E \left\langle \varphi_1 \left| -i \frac{\partial}{\partial t} \right| \varphi_E \right\rangle \times \exp \left[-i \int_0^t (E - E_1) dt' \right],$$

$$i \frac{da_2}{dt} = a_1 \left\langle \varphi_2 \left| -i \frac{\partial}{\partial t} \right| \varphi_1 \right\rangle \exp \left[-i \int_0^t (E_1 - E_2) dt' \right], \quad (20)$$

$$i \frac{da_E}{dt} = a_1 \left\langle \varphi_E \left| -i \frac{\partial}{\partial t} \right| \varphi_1 \right\rangle \exp \left[-i \int_0^t (E_1 - E) dt' \right]$$

using a Gauss-Laguerre quadrature for the energy, and a Burlisch-Stoer²⁹ integration for the time.

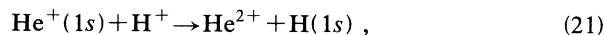
Figure 4(a) shows that when the two-state approximation is adequate ($v \leq 1$ a.u.), approximate and exact treatments yield the same answer, as they should. For $v=1.5$ [Fig. 4(b)], the effect of P - Q couplings is sizable, and for $v=2$ [Fig. 4(c)] “ionization” ($\varphi_1 \rightarrow \varphi_E$) dominates “charge exchange” ($\varphi_1 \rightarrow \varphi_2$); in both cases addition of a single ra-

dial derivative function $\varphi_1^{(1)}$ to the basis considerably improves P_2 . Finally, for $v=3$ a.u. [Fig. 4(d)] the “ionization” cross section is an order of magnitude larger than the “charge-exchange” one; then transitions to the continuum are so important that adding $\varphi_1^{(1)}$ to the basis causes the method to “overshoot,” and even addition of $\varphi_1^{(2)}$ is insufficient to significantly increase the accuracy of the method.

We have plotted the behavior of the state population $|a_2(t)|^2$ as a function of time—the “collision history”—for an impact parameter of $b=1$ a.u., in Figs. 6(a) ($v=1$), 6(b) ($v=1.5$), 6(c) ($v=2$), and 6(d) ($v=3$). Transitions from φ_1 to φ_2 occur with a large probability both for the way-in ($t < 0$) and for the way-out ($t > 0$) stages of the collision, which is a reasonable situation at intermediate nuclear velocities; we notice that such a model is sensitive to mechanisms that decrease the population of either channel by even a small amount. Most importantly, when agreement between exact and approximate results holds (namely, when $v < 3$ for P_2), it does so along the whole nuclear trajectory. We believe this excludes fortuitous agreement between exact and approximate probabilities. In fact, as could be expected from Eq. (9), the error in our approximate treatments is cumulative during the collision, and can be traced to the substitution of a single energy phase (or two phases when $\varphi_1^{(2)}$ is also included) for the nondenumerable amount of them that appear in Eq. (20). Finally, we notice from Fig. 6 that inclusion of Q states in the basis always changes the population of φ_2 in the correct direction, and that $v=3$ a.u. is a sufficiently high velocity that there begin to appear Stuckelberg-type oscillations in $|a_1(t)|^2$ from couplings to the continuum. Even though the magnitude of this entrance channel population is not well approximated at that high energy by our treatment, it is noteworthy that it does reproduce the oscillation effect.

IV. CHARGE EXCHANGE IN $\text{He}^+ + \text{H}^+$ COLLISIONS

As a second illustration, we have calculated the cross sections for the reaction



choosing as the basis of the P functions the set of HeH^{2+} molecular orbitals (MO's):

$$1s\sigma, 2s\sigma, 2p\pi, 3p\sigma, 3d\sigma, \quad (22)$$

$$3d\pi, 4f\sigma, 5g\sigma, \text{ and } 4f\pi,$$

multiplied by the CTF of Errea, Méndez, and Riera²⁸ with the choice of parameters $p_0=0.44$ and $\beta=3.5$. We present in Fig. 7 the cross section obtained with this molecular basis (22) and with the augmented one obtained by adding to it the orthogonalized radial components $\varphi_k^{(R)}$:

$$1s\sigma^{(R)}, 2p\pi^{(R)}, 4f\pi^{(R)}, \text{ and } 5g\sigma^{(R)}. \quad (23)$$

These values are compared in Fig. 7 to accurate theoretic-

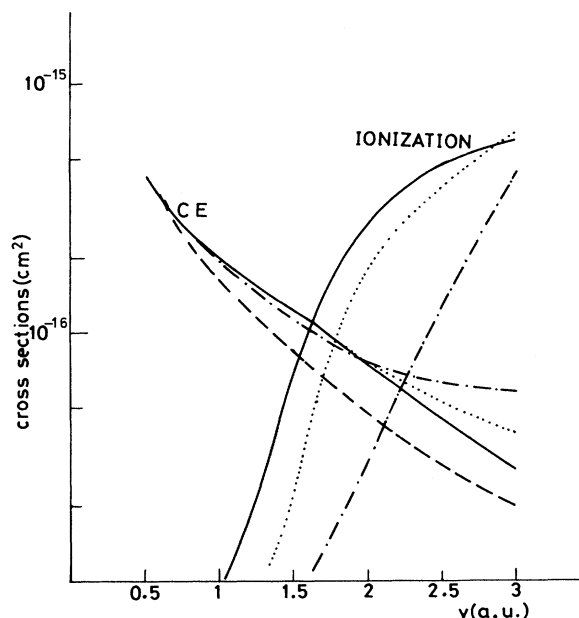


FIG. 5. “Charge-exchange” (CE) and “ionization” cross sections as functions of the impact velocity. Same symbols as in Fig. 4.

cal³⁰⁻³⁵ data. We have checked that rotational $\varphi_k^{(\theta)}$ and $O(v^2)$ components, as well as radial derivatives of other MO's in (i), are not important for the energy range considered. In fact, the number and kind of Q functions to be incorporated, as well as their properties, strongly depend on the P basis included. For example, with a single P function, $1s\sigma^{(R)}$ tends to reproduce the $2p\sigma$ orbital plus ionizing and other components; with the full basis (22) the Q operator in (10) then projects out the $2p\sigma$ orbital from $1s\sigma^{(R)}$, and singles out the other components;

similarly, $2p\sigma^{(R)}$ partly tends to reproduce $3d\sigma$ when this MO is not included in the basis; $3d\sigma^{(R)}$ is close to $4f\sigma$; $4f\sigma^{(R)}$ partly describes $5g\sigma$, and so on. The energies and couplings corresponding to the adiabatic states (i) are well known, and will not be presented; those for the radial derivatives (ii) are displayed in Figs. 8 (energies) and 9 ($\varphi_k - \varphi_k^{(R)}$ couplings).

The P - Q couplings were evaluated by accurate sum-over-pseudostates expressions as explained in Ref. 11. On the other hand, since the accuracy of these expres-

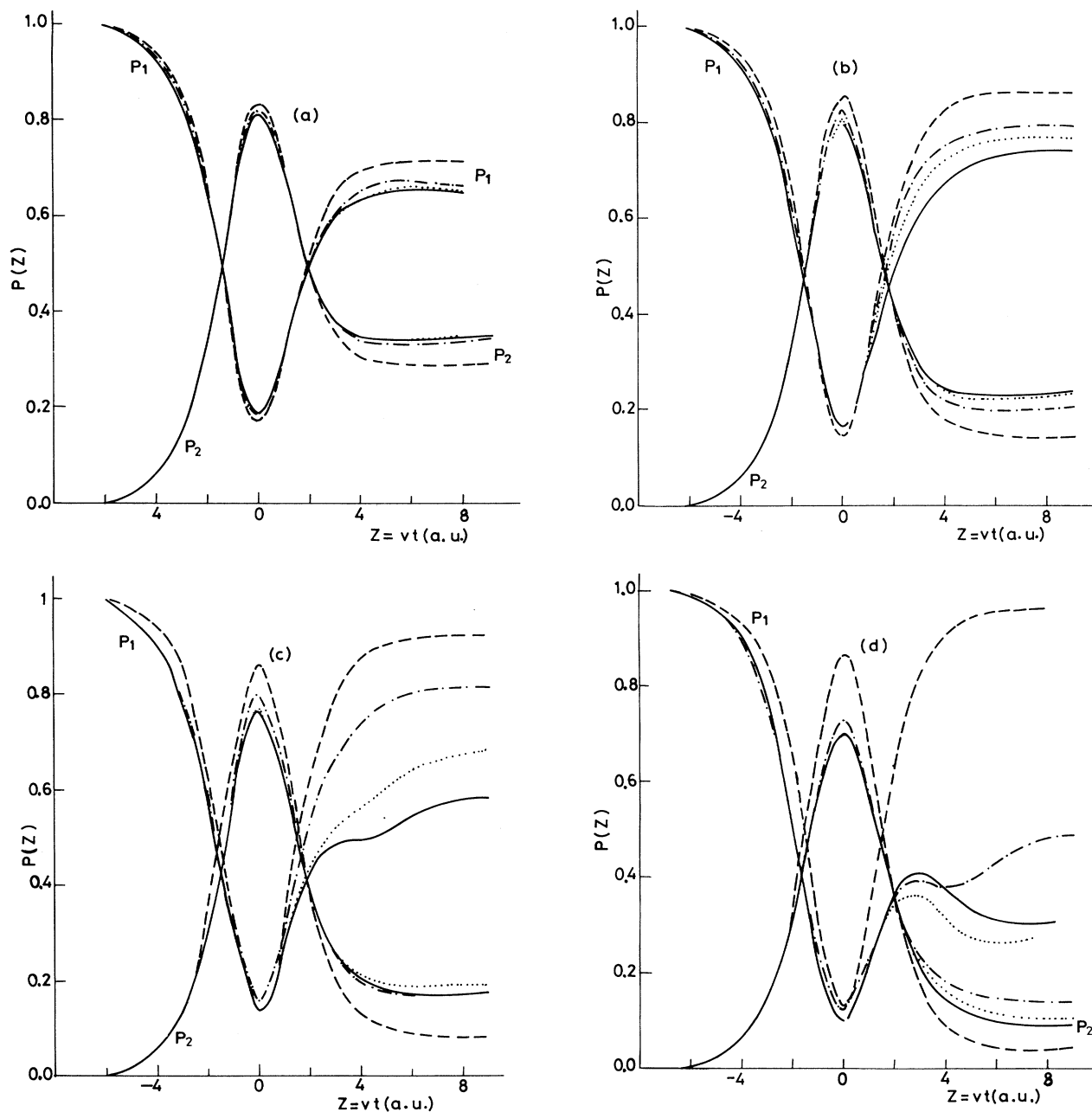


FIG. 6. Population of the adiabatic wave functions φ_1, φ_2 as a function of $Z=vt$, for a nuclear trajectory with impact parameter $b=1.0$ a.u. and different values of the impact velocity: (a) $v=1.0$ a.u.; (b) $v=1.5$ a.u.; (c) $v=2.0$ a.u.; (d) $v=3.0$ a.u. Same symbols as in Fig. 4.

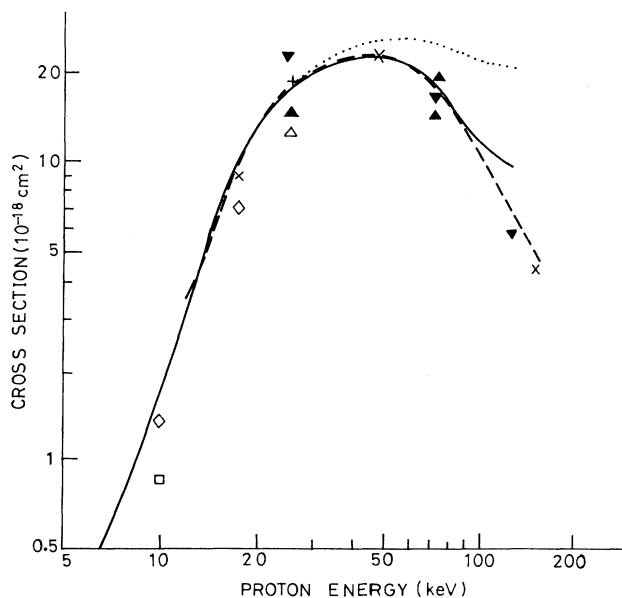


FIG. 7. Cross sections (10^{-18} cm^2) for the $\text{He}^+(1s) + \text{H}^+ \rightarrow \text{He}^{2+} + \text{H}(1s)$ reaction, as a function of the proton energy (in keV). Present calculations: \cdots , ten molecular orbital basis set of Eq. (22); — , basis set augmented by adding the four orbitals of Eq. (23). Other results: \diamond , Winter, Hatton, and Lane (Ref. 30); \square , Kimura and Thorson (Ref. 31); \times , Winter (Refs. 36 and 38); $+$, Winter (Ref. 39); --- , Fritsch and Lin (Ref. 37); \blacktriangledown , Reading, Ford, and Becker (Ref. 32); \triangle , \blacktriangle , Bransden, Noble, and Chandler (Ref. 35).

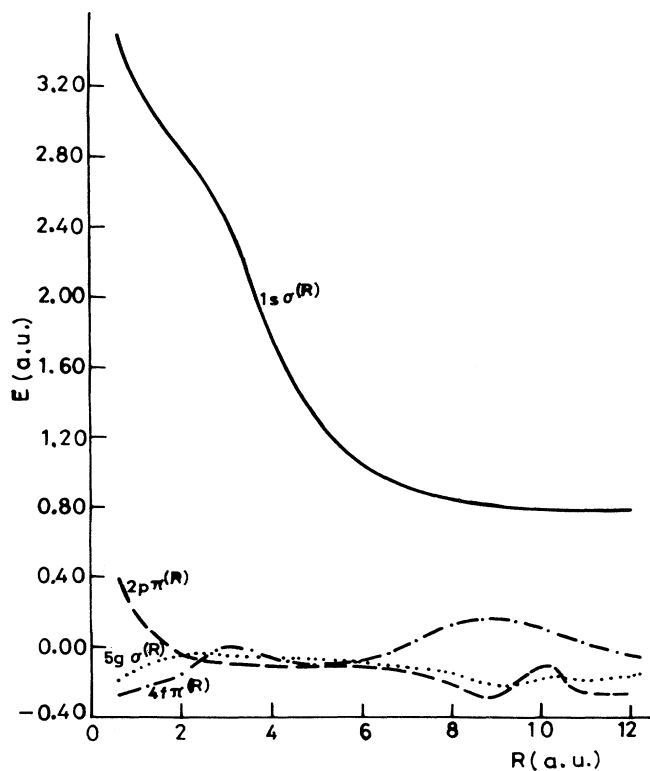


FIG. 8. Expectation values of the electronic Hamiltonian for the four radial components $\varphi_k^{(R)}$ of Eq. (23) as functions of the internuclear distance.

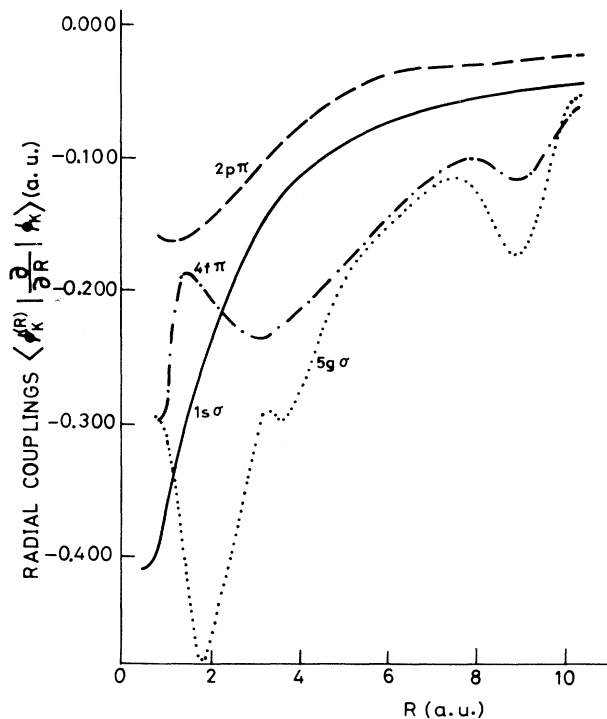


FIG. 9. Radial couplings $\langle \varphi_k^{(R)} | \partial / \partial R | \varphi_k^{(R)} \rangle$ as functions of the internuclear distance.

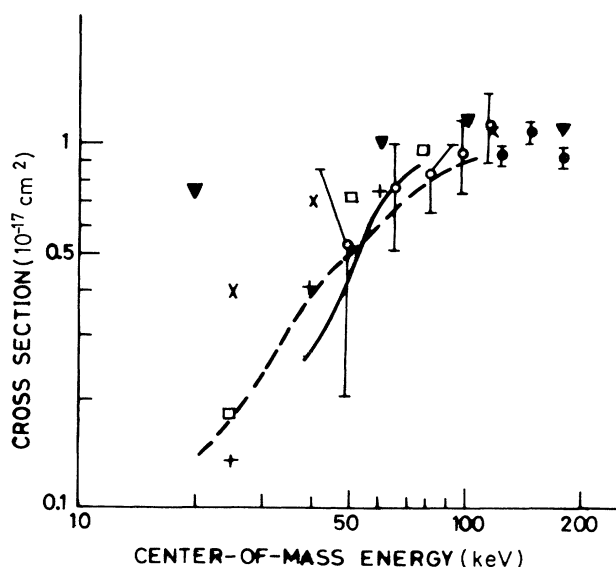
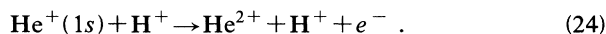


FIG. 10. Cross sections (10^{-17} cm^2) for the $\text{He}^+(1s) + \text{H}^+ \rightarrow \text{He}^{2+} + \text{H}^+ + e^-$ reaction, as a function of the center-of-mass energy (in keV). Present calculations: --- , Winter (Ref. 39); $+$, Winter (Refs. 36 and 38); \square , Fritsch and Lin (Ref. 37); \blacktriangledown , Reading, Ford, and Becker (Ref. 32). Experiment: \odot , Watts, Dunn, and Gilbody (Ref. 42); \oplus , Angel *et al.* (Ref. 40) as corrected in Ref. 42; — , Peart, Rinn, and Dolder (Ref. 41).

sions for Q - Q couplings is difficult to ascertain and transition probabilities to derivative functions were seen to be very small, we have neglected these couplings in the present calculations. Numerical integration of the set of differential equations for the expansion coefficients was performed, as for the previous illustration, with the program PAMPA,²⁹ modified so as to include the corrections due to the translation factor.

The main purpose of this second illustration is to show that our proposed method can be implemented, and is not restricted to "easy" examples such as those of Sec. III. On the other hand, since the exact behavior of the electronic wave function is unknown, it provides less information on the pointwise approximations obtained. It is therefore encouraging that our results follow the same trend as in the previous example. From Fig. 7 we see that addition of the derivative functions (23) is able to improve the behavior of the charge-exchange cross section beyond its maximum; in this respect, it may be remarked that addition of four adiabatic states to the basis does not lead to a noticeable improvement of that curve. We notice that the highest nuclear velocity considered in the present work is superior to that of the electron in the initial $\text{He}^+(1s)$ orbital, so that ionization fully competes with charge exchange at this velocity. Then, probability flux towards Q space is no longer a small correction to the molecular method and 14-term treatment begins to break down. In Fig. 10 we show that our calculated cross section for exit through the derivative functions closely agrees with theoretical^{32,36-39} and experimental⁴⁰⁻⁴² results for the ionization process:



Nevertheless, since those functions have a component of higher-lying bound states as well as continuum ones, and transitions to the former states do not necessarily lead, through ladder-type processes, to ionization, our results in Fig. 10 must be interpreted as upper-bound estimates to the ionization cross section. As mentioned in Sec. II this ambiguity in the interpretation of probability ending up in absorber states is intrinsic to our approach.

We finally plot, as for the previous example, in Figs. 11(a) ($v = 3^{1/2}$) and 11(b) ($v = 5^{1/2}$) charge-exchange transition probabilities calculated with the bases (22) and (22)+(23), as functions of the impact parameter b , together with the corresponding ionization probability

V. CONCLUSION

The molecular model (generalized by the introduction of translation factors) fails to describe charge-exchange cross sections when couplings to an infinite number of (Rydberg and) ionizing states, spanning what we have called Q space, are effective. Accordingly, when ionization cannot be neglected, a departure from this usual molecular treatment is required but, when v is not too high, it seems reasonable that the departure need not be a drastic one. In this work we have proposed to approximate the probability flux towards Q space by adding to the molecular expansion some representative (nonadiabatic) wave functions, defined so as to absorb all direct

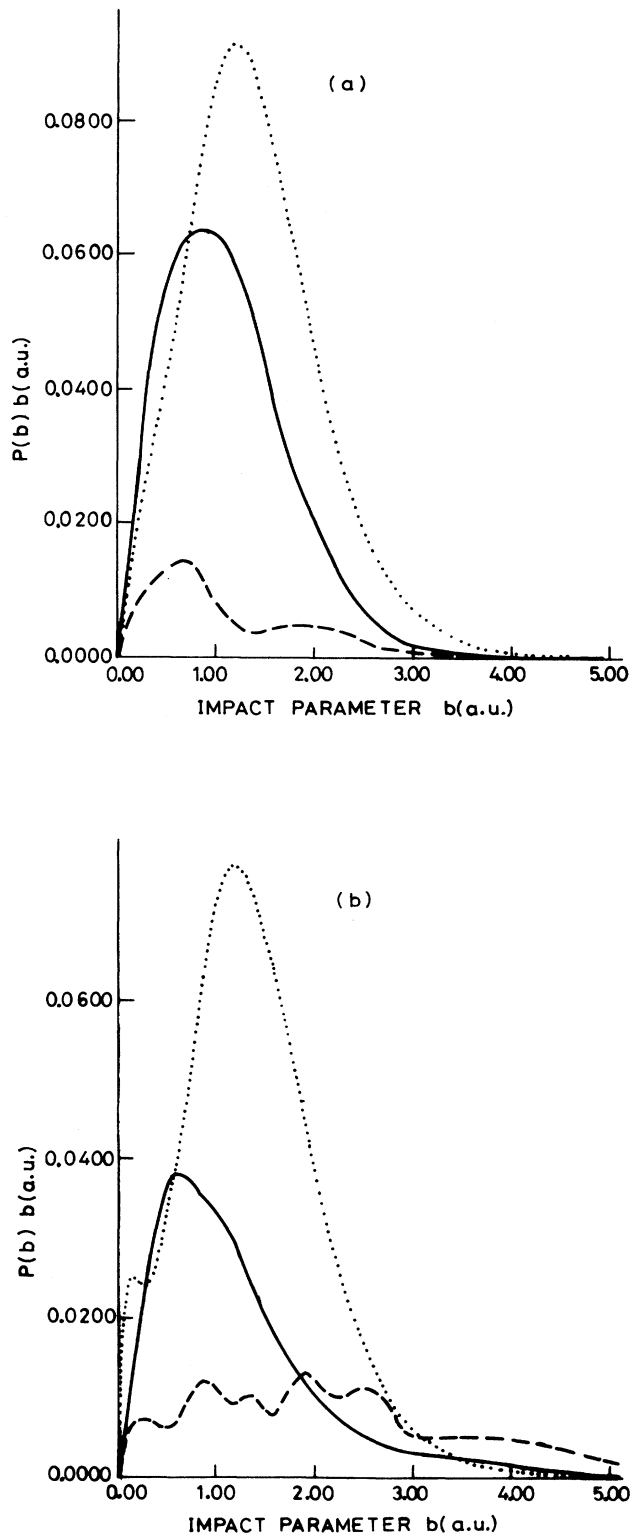


FIG. 11. Transition probabilities $P(b)$ times the impact parameter b : \cdots , charge-exchange results obtained with the basis set of Eq. (22); — , charge-exchange results obtained with the basis set of Eqs. (22) and (23); --- , ionization results. (a) $v = 3^{1/2}$ a.u., (b) $v = 5^{1/2}$ a.u.

probability leakage from states included in the molecular expansion.

To check the degree of accuracy and limitations of the method for a case where transition probabilities can be calculated exactly, we have set up a model system, and compared exact and approximate channel populations as functions of time and impact parameter. For this model system, the method was seen to perform as desired. Its main limitation is that phase effects due to discrete-continuum energy differences are difficult to reproduce by

adding a few terms to the basis. An application to the benchmark case of He^+H^+ collisions is also presented, and yields encouraging results as to the implementation of our new approach to atomic collision problems.

ACKNOWLEDGMENTS

This research has been partially supported by the Dirección General de Investigación Científica y Técnica Project No. PB87-0112, and European Economic Community (EEC) twinning project SCI*.0138.C(JR).

- ¹D. R. Bates, H. S. W. Massey, and A. L. Steward, Proc. R. Soc. London Ser. A **216**, 437 (1953).
- ²D. R. Bates and R. McCarroll, Proc. R. Soc. London Ser. A **245**, 175 (1958).
- ³W. R. Thorson and J. B. Delos, Phys. Rev. A **18**, 117 (1978); **18**, **135**, (1978).
- ⁴J. B. Delos, Comments At. Mol. Phys. **10**, 211 (1981); Rev. Mod. Phys. **53**, 287 (1981).
- ⁵A. Riera, Comments At. Mol. Phys. **12**, 95 (1982).
- ⁶A. Macías and A. Riera, Phys. Rep. **90**, 299 (1982).
- ⁷A. Riera, Phys. Rev. A **30**, 2304 (1984).
- ⁸L. F. Errea, J. M. Gómez Llorente, L. Méndez, and A. Riera, Phys. Rev. A **32**, 2158 (1985).
- ⁹L. F. Errea, J. M. Gómez Llorente, L. Méndez, and A. Riera, Phys. Rev. A **35**, 4060 (1987).
- ¹⁰L. F. Errea, J. Gómez Llorente, L. Méndez, A. Riera, C. Harel, and H. Jouin, Europhys. Lett. **6**, 391 (1988).
- ¹¹L. F. Errea, L. Méndez, and A. Riera, Phys. Rev. A **39**, 2404 (1989).
- ¹²L. F. Errea, L. Méndez, and A. Riera, Z. Phys. D **14**, 229 (1989).
- ¹³R. J. Allan and H. J. Korsch, Z. Phys. A **320**, 191 (1985); M. Bendahman, S. Bliman, S. Dousson, D. Hitz, R. Gayet, J. Hanssen, C. Harel, and A. Salin, J. Phys. (Paris) **46**, 561 (1985); R. J. Allan, J. Phys. B **19**, 1891 (1985); R. J. Allan, A. Bahring, and J. Hanssen, *ibid.* **18**, 1994 (1985); S. A. Blanco, C. A. Falcón, C. O. Reinhold, J. I. Casaubón, and R. D. Piacentini, *ibid.* **20**, 6295 (1987); M. Gargaud, R. McCarroll, and P. Valiron, *ibid.* **20**, 1555 (1987); L. Opradolce, L. Benmeuraim, R. McCarroll, and R. D. Piacentini, *ibid.* **21**, 503 (1988); M. Gargaud and R. McCarroll, *ibid.* **21**, 513 (1988); M. Gargaud, R. McCarroll, and L. Opradolce, *ibid.* **21**, 521 (1988).
- ¹⁴L. F. Errea, L. Méndez, A. Riera, M. Yáñez, C. Harel, J. Hanssen, and A. Salin, J. Phys. (Paris) **46**, 719 (1985); F. Martín, A. Riera, and M. Yáñez, Phys. Rev. A **34**, 467 (1986); R. J. Allan, J. Phys. B **19**, L683 (1986); F. Martín, A. Riera, and M. Yáñez, J. Chem. Phys. **84**, 5422 (1986); M. Terao, S. Szücs, M. Cherkani, F. Brouillard, R. J. Allan, C. Harel, and A. Salin, Europhys. Lett. **1**, 123 (1986); O. Mó and A. Riera, J. Phys. B **21**, 119 (1988); L. F. Errea, L. Méndez, and A. Riera, Phys. Scr. **T28**, 67 (1989); S. Osimitsch, W. Jitschin, H. Reihl, H. Kleinpoppen, H. O. Lutz, O. Mó, and A. Riera, Phys. Rev. A **40**, 2958 (1989); C. Harel and H. Jouin, Europhys. Lett. **11**, 121 (1990).
- ¹⁵C. W. Newby, J. Phys. B **18**, 1781 (1985).
- ¹⁶L. F. Errea, L. Méndez, and A. Riera, Chem. Phys. Lett. **164**, 261 (1989).
- ¹⁷D. A. Micha and R. D. Piacentini, Phys. Rev. A **25**, 204 (1982); T. H. J. de Reus, J. Reinhardt, B. Muller, W. Greiner, G. Soff, and U. Muller, J. Phys. B **17**, 615 (1984).
- ¹⁸G. Bandarage and W. R. Thorson, Phys. Rev. A **37**, 692 (1988).
- ¹⁹G. Bandarage and W. R. Thorson, Phys. Rev. A **37**, 716 (1988).
- ²⁰H. J. Lüdde, H. Ast, and R. M. Dreizler, J. Phys. B **21**, 4131 (1988); Z. Phys. **15**, 141 (1989).
- ²¹H. Ast, H. L. Lüdde, and R. M. Dreizler, J. Phys. B **21**, 4143 (1988).
- ²²H. J. Lüdde and R. M. Dreizler, J. Phys. B **22**, 3243 (1989).
- ²³H. Feshbach, Ann. Phys. (N.Y.) **5**, 357 (1958); **19**, 287 (1962).
- ²⁴L. Spruch, in *Lectures in Theoretical Physics: Atomic Collisions*, edited by S. Geltman, K. T. Mahanthappa, and V. B. Britten (Gordon and Breach, New York, 1968); C. Chang and D. Rapp, Phys. Rev. A **8**, 193 (1973); D. Storm, *ibid.* **10**, 1008 (1974); D. Storm and D. Rapp, *ibid.* **14**, 193 (1976).
- ²⁵S. B. Schneidermann and A. Russek, Phys. Rev. **181**, 1311 (1969).
- ²⁶G. Wannier, Phys. Rev. **52**, 191 (1937).
- ²⁷P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).
- ²⁸L. F. Errea, L. Méndez, and A. Riera, J. Phys. B **15**, 101 (1982).
- ²⁹C. Gaussorgues, R. D. Piacentini, and A. Salin, Comput. Phys. Commun. **10**, 2241 (1975).
- ³⁰T. G. Winter, G. J. Hatton, and N. F. Lane, Phys. Rev. A **22**, 930 (1980).
- ³¹M. Kimura and W. R. Thorson, Phys. Rev. A **24**, 3019 (1981).
- ³²J. F. Reading, A. L. Ford, and R. L. Becker, J. Phys. B **15**, 625 (1982).
- ³³T. G. Winter, Phys. Rev. A **25**, 697 (1982).
- ³⁴W. Fritsch and C. D. Lin, J. Phys. B **15**, 1255 (1982).
- ³⁵B. H. Bransden, C. J. Noble, and J. Chandler, J. Phys. B **16**, 4191 (1983).
- ³⁶T. G. Winter, Phys. Rev. A **33**, 3842 (1986).
- ³⁷W. Fritsch and C. D. Lin, in *Abstracts of the Twelfth International Conference on the Physics of Electronic and Atomic Collisions*, Gatlinburg, 1982, edited by J. Eichler, W. Fritsch, I. V. Hertel, N. Stolterfoht, and U. Wille (North-Holland, Amsterdam, 1983), p. 502.
- ³⁸T. G. Winter, Phys. Rev. A **35**, 3799 (1987).
- ³⁹T. G. Winter, Phys. Rev. A **37**, 4656 (1988).
- ⁴⁰G. C. Angel, E. C. Sewell, K. F. Dunn, and H. B. Gilbody, J. Phys. B **11**, L297 (1978).
- ⁴¹B. Peart, K. Rinn, and K. T. Dolder, J. Phys. B **16**, 1461 (1983).
- ⁴²M. F. Watts, K. F. Dunn, and H. B. Gilbody, J. Phys. B **19**, L355 (1986).