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Regularization of Coulomb potentials in the treatment of nonresonant transitions to an ionizing continuum

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Close-coupling techniques often break down when transitions to a continuum or quasicontinuum cannot be neglected. This work describes an extension of a recently proposed method [L. F. Errea, L. Méndez, and A. Riera, Chem. Phys. Lett. **164**, 261 (1989)] to deal with such situations, when the coupling terms involve Coulomb potentials. A connection with the method of packet states is made, and a preliminary application of the method is presented.

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I. INTRODUCTION

A standard approach in the treatment of dynamical atomic and molecular systems is the close-coupling method. The corresponding basis functions are electronic eigenfunctions of some operator H_0, such as the following.

(i) The Born-Oppenheimer Hamiltonian $H_0=H$, describing the whole system for fixed nuclear positions. The ensuing adiabatic expansion yields the so-called supermolecular, or perturbed stationary states, approach [1].

(ii) The Hamiltonian describing only a part of the system, or the sum of such operators. The best known example is a one-center expansion. In this case, the eigenfunctions of H_0 form a complete set, although the procedure is often slowly convergent. Faster convergence can be achieved with two- (or more) center expansions.

(iii) The sum of projected Hamiltonians $H_0=\sum_i Q_i H Q_i$, where the eigenfunctions of each term $Q_i H Q_i$ have a specific character. The most common application of this approach is the construction of diabatic states [2,3].

With any of these choices, the spectrum of H_0 usually consists of a discrete and a continuum part. As the justification of the close-coupling hinges on the completeness of the set of eigenfunctions of H_0, the expansion must also include an integral over the non-L^2 integrable continuum "eigenfunctions." In practice, inclusion of this nondenumerable set of functions is usually avoided, as the couplings between them involve δ functions, and their construction and numerical manipulation are not simple.

Neglect of transitions to the continuum, however, is not always possible, well-known examples being the nonradiative decay from a discrete state to an adjacent continuum (or quasicontinuum), as occurs in energy transfer, intramolecular relaxation, unimolecular reactions, and autoionization phenomena. In these cases, the problem is usually solved by use of operators of the type III and extensions of the work of Feshbach [4] and Fano [5] to treat resonant (same energy) transitions between discrete and continuum states.

The treatment of nonresonant transitions to a continuum is much less standard, and although the Feshbach formalism is extendable [6–9] to this case, its implementation is rather involved. To deal with those transitions, the introduction of a set of "probability absorbers," which provide an optimal augmentation of the close-coupling basis, was proposed in a recent letter [10]. The procedure offers computational advantages as the new functions are L^2 integrable, so that the calculation of the corresponding energy values and coupling terms is simple. As a price for this simplification, dissociative transitions cannot be unambiguously separated from transitions to high-lying bound states. If such information is required, more refined procedures on the basis of the optical potential approach [9], or the method of continuum wave packets [11–15], have to be employed.

The method proposed in Ref. [10] was applied [16] to the treatment of atomic collisions at high impact energies, using a Hamiltonian of type I, so that transitions to the continuum are caused by nonadiabatic coupling terms. This application was most useful in elucidating [17] the ionization mechanisms in the molecular treatment of atomic collisions. The present work extends the method to cases where the coupling operators involve at least one Coulomb potential. Applications are the use of close-coupling expansions in terms of eigenfunctions of Hamiltonians of type II, as in the use of one-center expansions at low energies such that molecular effects are important.

A summary of the previous theory is presented in Sec. II A. In Sec. II B the difficulties that arise for Coulomb interactions are analyzed, and a solution is proposed via regularization of the potential. We then show in Sec. II C that this solution follows naturally from a more flexible definition of absorber wave functions. An illustration of the previous points and a preliminary application are presented in Sec. III. Atomic units are used except where otherwise stated.

II. THEORY

A. Absorber functions

We start from a truncated close-coupling expansion

$$\Phi=\sum_{j=1}^{J} a_j\phi_j \exp\left[-i\int E_j dt\right] , \tag{1}$$

where ϕ_j are eigenfunctions of a Hamiltonian H_0 (see previous section), multiplied, if necessary, by appropriate translation factors. When H_0 depends on the time (as in a semiclassical molecular approach [1]) so do the energies E_j. To calculate the expansion coefficients a_j, the ansatz (1) is substituted in the projected dynamical equation

$$POP\Phi\equiv P\left[H-i\frac{\partial}{\partial t}\right]P\Phi=0 , \tag{2}$$

where we define [13,18] the projector P onto the manifold spanned by the wave functions included in Eq. (1), and Q onto its complement:

$$P=\sum_{j=1}^{J}|\phi_j\rangle\langle\phi_j|, \quad Q=1-P . \tag{3}$$

We may compare (2) with the exact dynamical equation

$$O\Psi=\left[H-i\frac{\partial}{\partial t}\right]\Psi=0 , \tag{4}$$

or

$$POP\Psi=-POQ\Psi , \tag{5}$$

$$QOQ\Psi=-QOP\Psi . \tag{6}$$

The right-hand side in (6) yields a probability leakage from P to Q space; since this is not considered in (2), one usually chooses the P space such that the leakage is as small as possible. In turn, the resulting Q population influences that of the P functions through the right-hand side in Eq. (5). The operator QOP is thence responsible for $P\rightarrow Q$ and $Q\rightarrow P$ fluxes. A measure [18] of this interaction operator is given by its Euclidean norm

$$N^2=\sum_{j=1}^{J}N_j^2=\sum_{j=1}^{J}\|QOP\phi_j\|^2 , \tag{7}$$

which also defines the partial norm N_j corresponding to the jth state. Furthermore, the norm (7) yields [17] an average value for the difference between exact and approximate solutions of the dynamical equation.

The proposal of Ref. [10] concerns cases in which probability leakage to Q space cannot be neglected but individual transition probabilities from any given P function ϕ_j to Q states are small. It is then sufficient to introduce a global representative for Q space to account for these transitions. This representative was chosen to be of the form

$$\phi_j^{(1)}=\frac{QO\phi_j}{\|QO\phi_j\|} , \tag{8}$$

which fulfills

$$\langle\phi_j^{(1)}|0|\phi_j\rangle=N_j , \tag{9}$$

so that ϕ_j has a vanishing coupling with any Q function that is orthogonal to $\phi_j^{(1)}$, and augmentation of the basis $\{\phi_i;i=1,\ldots,J)$ by addition of $\phi_j^{(1)}$ yields a new partial norm $N_j'=0$. The function (8) acts, therefore, as an optimal probability absorber for the P function ϕ_j.

The method consists in augmenting the basis set $\{\phi_j;j=1,\ldots,J\}$ through the addition of selected absorber functions (8), so as to approximate the effect of the missing POQ term in (5). In principle, one could generate a series of absorbers of absorbers, etc., so as to render the procedure exact in the limit [10], but, as may be expected, the method is not practical if one has to go beyond first generation absorbers. Energies and couplings involving absorber functions are calculated [16,17] using either closure [18] or expansion techniques [19]. The very simplicity of the definition (8) implies that the method has limitations, two of which are discussed in the following sections.

B. Generalization for Coulomb couplings

For systems involving Coulomb potentials, the method of Ref. [10] is not easily applicable to Hamiltonians H_0, which do not contain all these potentials. The reason is that the corresponding r^{-1} singularities appearing in the operator O of (8) cause the absorber functions to have infinite energies and couplings. The same happens to higher generation absorbers for any Hamiltonian containing singular potentials. On the other hand, there is no difficulty for first generation absorbers when $H_0=H$ (type I Hamiltonian), because then the coupling operator QOP of Eq. (8) does not have any singularity.

To analyze the difficulty, we take $H_0\neq H$, and consider the neighborhood of a given nucleus whose Coulomb potential $-Z/r$ is not included in H_0. Given any P function ϕ_j, the corresponding Q-space representative is, near $r=0$, of the form

$$\phi_j^{(1)}=-Z\frac{Qr^{-1}\phi_j}{\|QO\phi_j\|} . \tag{10}$$

Although the denominator in (10) is finite, the singularity of $r^{-1}\phi_j$ in the numerator leads to divergent energies of the absorber state, as well as to infinite couplings of $\phi_j^{(1)}$ with other absorbers. Since $\phi_j^{(1)}$ can be written solely in terms of any set of functions spanning Q space, we are led to investigating which is the region of this functional space that is responsible for the singularity. For this, we expand $r^{-1}\phi_j$ in terms of the complete set of eigenfunctions of the atomic Hamiltonian

$$\left[-\tfrac{1}{2}\nabla^2-\frac{Z}{r}\right]\chi_n=\varepsilon_n\chi_n\ , \tag{11}$$

in the form

$$r^{-1}\phi_j=\sum_{n=1}^{\infty}\chi_n\langle\chi_n|r^{-1}|\phi_j\rangle+\int_0^{\infty}dk\chi_k\langle\chi_k|r^{-1}|\phi_j\rangle\ , \tag{12}$$

with $k=(2\varepsilon)^{1/2}$.

Since only the neighborhood of $r=0$ is studied, it suffices to consider the s-wave contribution to expansion (12). Furthermore, each term in the sum and each integral over a finite domain of (12) are regular functions at $r=0$. Hence, the unboundedness of the left-hand side must come either from the series limit $n\rightarrow\infty$ or from the integral limit $k\rightarrow\infty$ in the right-hand side. It is easy to see that the first outcome is impossible: in the integrand of $\langle\chi_n|r^{-1}|\phi_j\rangle$ the factor $r^2r^{-1}\phi_j$ takes non-negligible values in a finite domain of configuration space where χ_n decreases as $n\rightarrow\infty$; hence, the integral vanishes in this limit. Furthermore, we have [20]

$$\chi_n(r=0)=Z^{3/2}\pi^{-1/2}n^{-3/2}\ , \tag{13}$$

which shows that the series of Eq. (12) converges with n at $r=0$.

Turning now to the upper limit of the integral over continuum states in (12), we consider

$$S=\lim_{k_{\max}\rightarrow\infty}\int_{k_{\min}}^{k_{\max}}dk\ \chi_k\langle\chi_k|r^{-1}|\phi_j\rangle\ , \tag{14}$$

with $k_{\min}$ large, where χ_k are the Coulomb functions [1,21]:

$$\chi_k=2^{-1/2}\pi^{-1}ke^{-Z\pi/2k}e^{ikr}\times|\Gamma(1+Zk^{-1})|\,{}_1F_1(1+Zk^{-1},2,-2ikr)\ , \tag{15}$$

with Γ the gamma and ${}_1F_1(a,b;z)$ the confluent hypergeometric function [22]. Because of the Jacobian r^2 factor, the matrix element $\langle\chi_k|r^{-1}|\phi_j\rangle$ is determined by the range of integration (k^{-1},∞), where since k is large, we can use in the integrand the asymptotic form for χ_k:

$$\chi_k\underset{kr\rightarrow\infty}{\sim}2^{-1/2}\pi^{-1}r^{-1}\sin(kr+\sigma-Zk^{-1}\ln 2kr)\ , \tag{16}$$

where σ is the Coulomb phase shift [1]. Using integration by parts we can generate an asymptotic series in powers of k^{-1}:

$$\langle\chi_k|r^{-1}|\phi_j\rangle=Ak^{-1}+O(k^{-2})\ , \tag{17}$$

with $A=2^{3/2}\cos(1+\sigma)\phi_j(k^{-1})$. Substitution in (14) yields, for $k_{\min}$ large,

$$S(r)=A2^{-1/2}\pi^{-1}\lim_{k_{\max}\rightarrow\infty}\int_{k_{\min}}^{k_{\max}}dk\ e^{ikr}\,{}_1F_1(1,2,-2ikr)\ . \tag{18}$$

Two cases may then be considered. For $r=0$, since ${}_1F_1=1$ the integral diverges like $k_{\max}$. On the other hand, for $0<r\ll 1$ one can use for $k_{\min}\gg 1/r$ the asymptotic form

$${}_1F_1\underset{k\rightarrow\infty}{\sim}k^{-1}r^{-1}e^{-ikr}\sin(kr+\sigma)\ , \tag{19}$$

and the limit in Eq. (18) converges to a value that behaves like r^{-1}, and therefore also diverges in the limit $r\rightarrow 0$.

Equation (18) shows that the divergence of $r^{-1}\phi_j$ must be ascribed to the $k\rightarrow\infty$ limit in (12). However, the function (10) behaves like $Qr^{-1}\phi_j$ rather than like $r^{-1}\phi_j$ near $r=0$. Expanding the Q operator in this neighborhood in terms of the $\{\chi_n,\chi_k\}$ set then leads to an analogous treatment for the former function. In particular (14) is replaced by

$$QS=\lim_{k_{\max}\rightarrow\infty}\lim_{k'_{\max}\rightarrow\infty}\times\int_{k'_{\min}}^{k'_{\max}}dk'\int_{k_{\min}}^{k_{\max}}dk\chi_{k'}(r)\langle\chi_{k'}|Q|\chi_k\rangle\times\langle\chi_k|r^{-1}|\phi_j\rangle\ . \tag{20}$$

At $r=0$, this becomes, for $k_{\min},k'_{\min}$ large,

$$QS(0)=A2^{-1/2}\pi^{-1}\lim_{k_{\max}\rightarrow\infty}\lim_{k'_{\max}\rightarrow\infty}\times\int_{k'_{\min}}^{k'_{\max}}dk'\int_{k_{\min}}^{k_{\max}}dk\langle\chi_{k'}|Q|\chi_k\rangle\ . \tag{21}$$

This quantity only converges if

$$\lim_{k\rightarrow\infty}\lim_{k'\rightarrow\infty}kk'\langle\chi_{k'}|Q|\chi_k\rangle=0\ , \tag{22}$$

which usually means that $Q\equiv 0$; this is an uninteresting case because then the original close-coupling expansion would be exact.

The previous reasoning shows that absorber functions as defined in (8) have an unphysical character near any Coulomb singularity not contained in H_0 because they contain contributions from states with very high positive energies. In more practical terms, absorbers take very large values in a region near $r=0$ and are therefore unsuitable as basis functions in a close-coupling treatment because they represent ionizing states with very large energies. Since these states are physically inaccessible, their contribution to the absorber function should be eliminated in any meaningful definition. This can be implemented by replacing the infinite limit in (12) by a finite value $k_{\max}$. We are thus led to substituting the full Coulomb potential by a regularized one:

$$V\phi_j=\sum_{n=1}^{\infty}\chi_n\langle\chi_n|-Zr^{-1}|\phi_j\rangle+\int_0^{k_{\max}}dk\ \chi_k\langle\chi_k|-Zr^{-1}|\phi_j\rangle\ . \tag{23}$$

In practice, this potential is nonlocal and may be awkward to use. In Sec. III we shall compare this procedure to the implementation of a simpler, local regularization of the Coulomb potential.

The substitution of the potential $-Zr^{-1}$ by a regularized version may seem an *ad hoc* procedure to offset the unphysical character of the absorber functions (8) near $r=0$. We now show that it follows naturally from the improvement of the theory that is presented in the following section.

C. Generalization to partial absorber states

According to the definition (8), absorber functions are global representatives of Q space that bear no direct relationship to the asymptotic eigenstates of the total electronic Hamiltonian H. Consequently, exit probabilities to any of these exact Q space eigenstates cannot be easily calculated. In particular, transitions to high-lying Rydberg Q levels can only be approximately separated from ionization processes in the energy region where both processes compete with each other [16,17].

It is very easy to formally generalize the definition of absorber states so as to be able to calculate partial cross sections to a set of discrete and/or continuum eigenfunctions of H belonging to Q space. For this, we first take any set of functions $\{\psi_n,\psi_k\}$, covering Q space, that asymptotically tend to those eigenfunctions. For discrete (orthonormal) functions ψ_n we define the partial projector

$$Q_\alpha=Q\sum_{n=i_\alpha}^{i_{\alpha+1}-1}|\psi_n\rangle\langle\psi_n| , \tag{24}$$

where the upper limit $i_{\alpha+1}$ may be infinite. For continuum wave functions, we define

$$Q_\alpha=Q\int_{k_\alpha}^{k_{\alpha+1}}dk\,|\psi_k\rangle\langle\psi_k| \tag{25}$$

and

$$Q_{\alpha_{\max}}=Q\int_{k_{\max}}^{\infty}dk\,|\psi_k\rangle\langle\psi_k| . \tag{26}$$

Generalization for non-orthonormal functions and the definition when both discrete and continuum levels are simultaneously considered are obvious. We can now write the Q projector:

$$Q=\bigcup_{\alpha=1}^{\alpha_{\max}}Q_\alpha , \tag{27}$$

where the union symbol $\bigcup$ is written instead of a sum $\sum$ because the partial projectors need not be orthogonal.

Partial absorber functions are then defined

$$\phi_{j\alpha}^{(1)}=\frac{Q_\alpha O\phi_j}{\|Q_\alpha O\phi_j\|} . \tag{28}$$

This trivially generalizes our previous approach, since the original absorber $\phi_j^{(1)}$ is contained in the manifold spanned by the set $\{\phi_{j\alpha}^{(1)};\alpha=1,\ldots,\alpha_{\max}\}$. The finer the partition of Q in (27), the more information we can obtain from the dynamical calculation, at the cost, of course, of an increased computational effort.

In fact, in the limit of a very finite partition the definition (28) is excessively complicated, and the procedure then appears as a variant of the packet state methods defined by Reading *et al.* [13], Bandarage and Thorson [14], and Micha and Piacentini [15]. The former authors slice the ionizing continuum into slabs of width Δ_n, either to construct pseudostates that represent this continuum as a basis, or in the integral over the continuum spectrum which appears in the explicit form of the dynamical equation (5); in this latter case an energy damping function appears in the resulting weighting function, which effectively prevents transitions to highly excited ionizing states. In the treatment of Bandarage and Thorson [14], a weighting function due to electron escape appears when account is taken of the difference between the space spanned by the dynamical evolution of the packet states and that spanned by the original continuum molecular orbitals. Such damping and escape effects are not taken into account in the present formalism, which treats absorber and P states on the same footing, so that probability is strictly conserved; one possible drawback of this approach is that backflow from absorber to P states may be overestimated. Finally, the method of Micha and Piacentini is to generate a basis of orthonormal pseudostates, defined by integrations over the continuum wave functions with suitable weight functions; similarly to our proposal, no probability escape mechanism is described.

The definition (28) is most useful when the energy intervals of the partition (27) are large, and may formally be considered as a special case of nonorthogonal packet states in which the "weight" function ascribed to each (quasi-)continuum state is proportional to its coupling to ϕ_j. In this way, the approach is adapted to the situation in which one is able to describe most of the dynamics within P space, and one wishes to increase the accuracy of the method by allowing for transitions from selected P functions into Q space. Given a P function ϕ_j, the partial absorber functions then appear as an optimal choice for the packet states, in which the states involved are weighted according to the strength of their coupling to ϕ_j.

The present generalization has two further advantages over the previous one [10]. First, the method is formally more satisfactory in that it can treat resonant as well as nonresonant discrete-continuum interactions: in the limit of sufficiently narrow energy bands in Eq. (25), a perturbative approach for resonant $P\rightarrow Q$ transitions leads to an expression [23] for the dissociation probability that is equivalent to the known procedure of adding an imaginary potential $-i\Gamma/2$ (where Γ is the corresponding energy width [4,5]) to the Hamiltonian H_0 defining the autoionizing state.

Second, it provides a justification to the regularization procedure described in the preceding section. In the case treated in that section, the last term in (27) leads to a partial absorber

$$\phi_{j\alpha_{\max}}^{(1)}=\frac{Q_{\alpha_{\max}}O\phi_j}{\|Q_{\alpha_{\max}}O\phi_j\|} , \tag{29}$$

that is singular at $r=0$ and describes physically inaccessible states. In fact, the failure of the packet state method to account for transitions to ionizing states with very high energies was pointed out in Ref. [13]. For the present purpose, we see that this "failure" is, in fact, an asset, and that the present generalization is useful even in the simplest case where partial cross sections to Q functions are not required. Then, we can partition the Q operator

$$Q=Q_1 \cup Q_{\alpha_{\max}} \tag{30}$$

with $\alpha_{\max}=2$, and we can augment the basis with a physically meaningful absorber function, which, according to (24) and (25), is defined as in Eq. (8), with Q replaced by Q_1. Since

$$-ZQ_1 r^{-1}\phi_j = QV\phi_j \; , \tag{31}$$

this is equivalent to substituting in that definition any Coulomb potential not included in H_0 by a regularized form (23). The same applies to higher generation absorbers for any choice of H_0.

III. ILLUSTRATIONS

A. Regularizations of the Coulomb potential

We shall first illustrate the inconvenience of incorporating highly excited states in expansion (12), even when the continuum integral is substituted by a summation over discretized [13,24] functions. For this purpose, for the simplest heteronuclear system HeH^{2+}, we have drawn in Fig. 1 some electronic density contours for the function $-Qr^{-1}\phi_1$, where ϕ_1 is the $1s$ orbital of a He^+ ion situated at a distance 1.0 bohr from the proton $Q=1-|\phi_1\rangle\langle\phi_1|$ and r is the distance from the proton. Figure 2 shows the behavior of the approximate absorber near $r=0$:

$$-Qr^{-1}\phi_1 \simeq -Q\sum_{n=1}^{8}\chi_n\langle\chi_n|r^{-1}|\phi_1\rangle \\ -Q\sum_{\lambda=1}^{5}\chi_\lambda\langle\chi_\lambda|r^{-1}|\phi_1\rangle \; , \tag{32}$$

which is written as a superposition of eight bound orbitals χ_n of s symmetry, and five discretized s-wave continuum orbitals χ_λ that were obtained in a variational calculation for the H atom. Exact (Fig. 1) and approximate (Fig. 2) absorber functions exhibit similar characteristics in the neighborhood of $r=0$, only the exact one being, of course, strictly singular at this point.

Next, to show that the behavior near $r=0$ is due to the contribution from highly excited continuum states, we display in Fig. 3 the contours obtained by eliminating the two orbitals χ_λ with the highest energies ($\varepsilon=25$ and 125 hartrees) in (32). Those orbitals have energies that are inaccessible in most physical situations, and their elimination leads to an absorber that is smoother than that of Fig. 2, and is therefore more useful as a basis function in a close-coupling expansion. A direct comparison between the functions of Figs. 1, 2, and 3 is given in Fig. 4, where we have plotted the values of these functions along the internuclear axis.

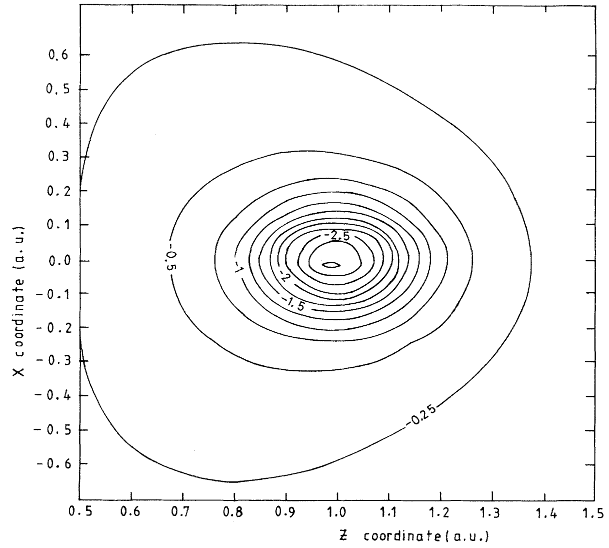

FIG. 1. Electronic density contours for the (unnormalized) exact absorber function $-Qr^{-1}\phi_1$ [see Eq. (10) of text], where ϕ_1 is the $\mathrm{He}^+(1s)$ target orbital, r is the electronic coordinate with respect to the proton location, and $Q=1-|\phi_1\rangle\langle\phi_1|$. The internuclear distance is of 1.0 bohr, and z coordinates are taken along the internuclear axis, with origin at the target (He^+) nucleus.

It should be stressed that the regularization of the Coulomb potential thus achieved is far from being unique: there is a wide choice in the value of $k_{\alpha_{\max}}$ in the definition of Q_1 of Eqs. (30) and (31). This choice plays a similar role to that of basis selection in bound-state problems. The smaller the value of $k_{\max}$, the smoother the corresponding absorber function, but when $k_{\max}$ is

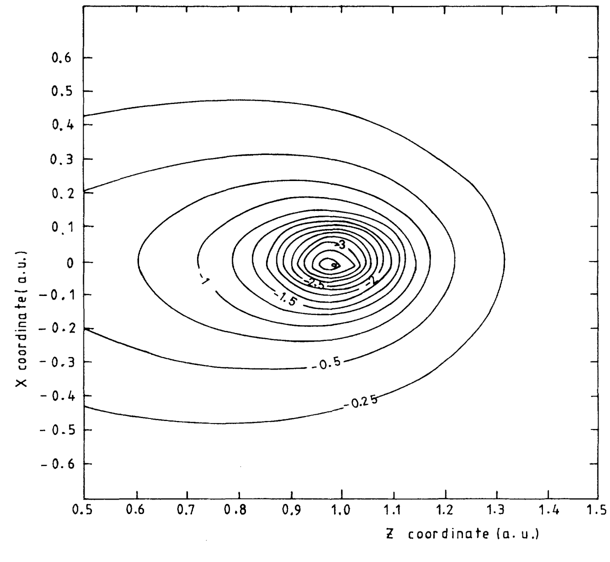

FIG. 2. Electronic density contours for the approximate absorber $-Qr^{-1}\phi_1$, defined in Eq. (32) of text, in terms of 13 orbitals obtained in a diagonalization of the H Hamiltonian in a basis. Conventions as in Fig. 1.

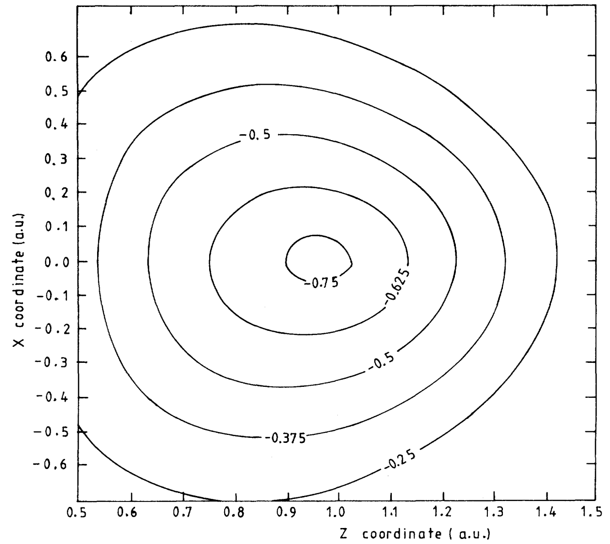

FIG. 3. Electronic density contours for the regularized absorber of Eq. (32) of text, obtained by eliminating the two highest excited orbitals in the expansion.

chosen to be too small this function may no longer represent all ionizing states that are accessible during the collision. Clearly, the method is useful when results are not critically dependent on the type of regularization employed. Otherwise, one should either increase the amount of P states or define a finer grid of partial absorbers (see Sec. III C).

To illustrate the choice of $k_{\max}$ in the regularization procedure, we choose a neighborhood of $r=0$ such that the function ϕ_j can be considered as approximately constant in (23):

$$V \simeq \sum_{n=1}^{8} \chi_n \langle \chi_n | -Zr^{-1} \rangle + \sum_{\lambda=1}^{\lambda_{\max}} \chi_\lambda \langle \chi_\lambda | -Zr^{-1} \rangle . \qquad (33)$$

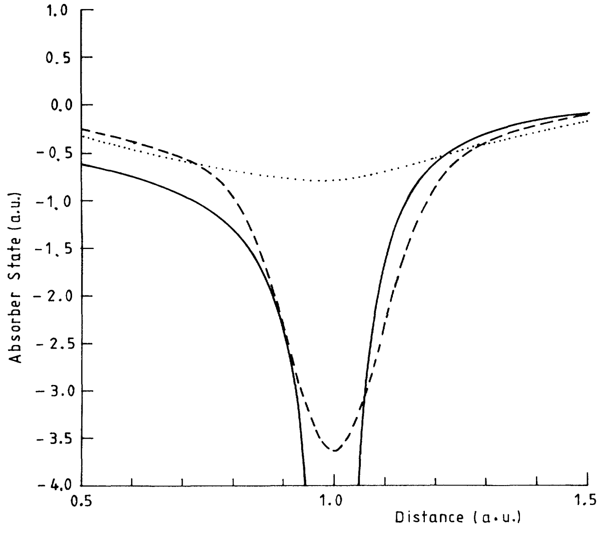

FIG. 4. Comparison between the values taken by the absorber functions of Figs. 1 (——), 2 (— — —), and 3 (· · · ·) along the internuclear axis.

We have drawn in Fig. 5, as a function of the distance from the H nucleus along the internuclear axis, the result of taking $\lambda_{\max}=0-5$ in (33). It may be noticed that the curves asymptotically ($r \gg 0$) coincide because the form of the absorbers is dominated in that region by the excited bound orbitals in (33).

Next, we compare the previous nonlocal regularization with a simpler local procedure. We have drawn in Fig. 6 the values for the potentials

$$V = -Zr^{-1}(1-e^{-\mu r}) , \qquad (34)$$

which depend on a parameter μ, such that in the limit $\mu \rightarrow \infty$ we obtain the original Coulomb singularity. Comparison between Figs. 5 and 6 shows the overall (though not point-to-point) similarity between both sets of regularized potentials, from the point of view of defining absorber states according to Eq. (8).

B. Dynamical calculations

We present here a preliminary account of the results of applying the new method to a one-center treatment of $H^+ + He^+(1s)$ collisions, in the framework of an impact-parameter semiclassical formalism. A full description of the calculations, as well as an application to the whole range of energies and to more benchmark cases, will be reported elsewhere. The functional space employed in the calculations is spanned by ten target (He^+) orbitals of lowest energy and the corresponding ten absorber states, which are defined by

$$\phi_j^{(1)} = \frac{QV\phi_j}{\|QV\phi_j\|} , \qquad (35)$$

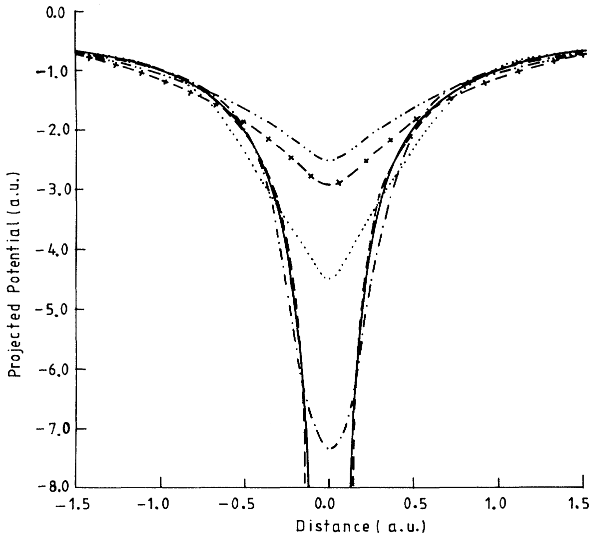

FIG. 5. Illustration of the behavior of exact and nonlocal regularized Coulomb potentials [Eq. (33) of text], as functions of the distance from the H nucleus along the z (internuclear) axis. ——, bare $-r^{-1}$ Coulomb potential; — — —, $\lambda_{\max}=5$; —·—·—·, $\lambda_{\max}=4$; · · · ·, $\lambda_{\max}=3$; —+—+—, $\lambda_{\max}=2,1$; —··—··—, $\lambda_{\max}=0$.

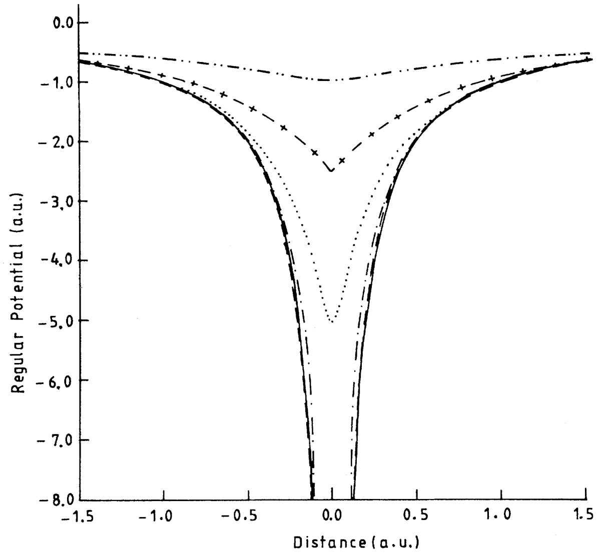

FIG. 6. Illustration of the behavior of exact and local regularized Coulomb potentials [Eq. (34) of text], as functions of the distance from the *H* nucleus along the *z* (internuclear) axis. ——, bare $-r^{-1}$ Coulomb potential; — — —, $\mu=150$; —·—·—·, $\mu=10$; · · · ·, $\mu=5$; —+—+—, $\mu=2.5$; —..——..—, $\mu=1.0$.

where V is the regularized potential of Eq. (34). For the present purpose, it suffices to give the results for some representative collision energies and μ values.

We compare in Fig. 7 our electron-loss (charge transfer plus ionization) cross sections with those of accurate capture and ionization calculations [25] and with experimental data [26–28]. The corresponding excitation cross sections into $He^+(2s,2p)$ are given in Fig. 8. Since, to our knowledge, there are no experimental data available for excitation, the present results can only be compared to those of previous two-center calculations [29].

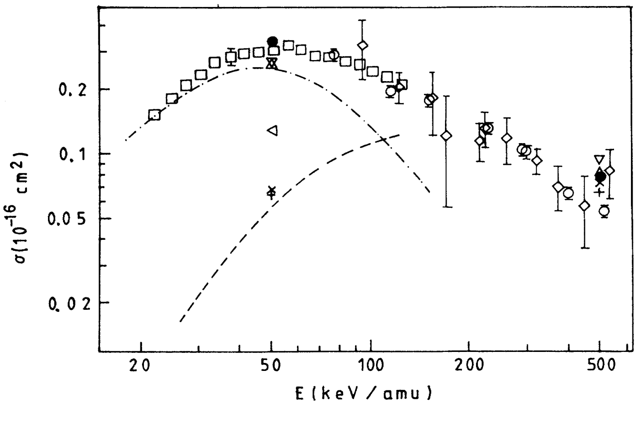

FIG. 7. Electron-loss cross section for $He^+(1s)+H^+$ collisions, calculated with the regularized potential (34) of text, with △, $\mu=1$; ●, $\mu=2.5$; ▽, $\mu=5$; ◁, $\mu=10$; ×, $\mu=50$; +, $\mu=150$. Previous theoretical calculations of Winter [25] corresponding to the ionization cross section (— — —) and to the electron-capture cross section (—·—·—·). Electron-loss experimental data: □, Rinn *et al.* [26]; ◇, Mitchell *et al.* [27]; ○, Angel *et al.* [28].

As explained above, to separately obtain results that can be unambiguously ascribed to charge transfer or ionization, we should improve our treatment by introducing partial absorber states in the close-coupling basis. This was not done in the present calculations. Nevertheless, by extending our previous reasonings, both cross sections can be separately calculated to a reasonable approximation through use of different values of the regularization parameter μ as follows.

(i) For large values of μ (≥ 50) the potential (34) is very close to the Coulomb one except for a negligible neighborhood of the projectile. Then, the absorbers (10) describe, near $r=0$, high energy inaccessible continuum states. On the other hand, they are regular near the target, where they describe excited and continuum target states. Therefore, for large values of μ, our calculation should be able to reproduce both target excitation and target ionization, though not charge exchange. This is exemplified in Fig. 9, where it is shown that as μ increases the calculated cross sections for electron loss converge to the ionization cross section, which is mostly due to target ionization as shown by electron spectra. The failure to reproduce charge exchange is especially noticeable at small energies (Fig. 7). On the other hand, the calculated excitation cross section is almost independent of μ (Fig. 8).

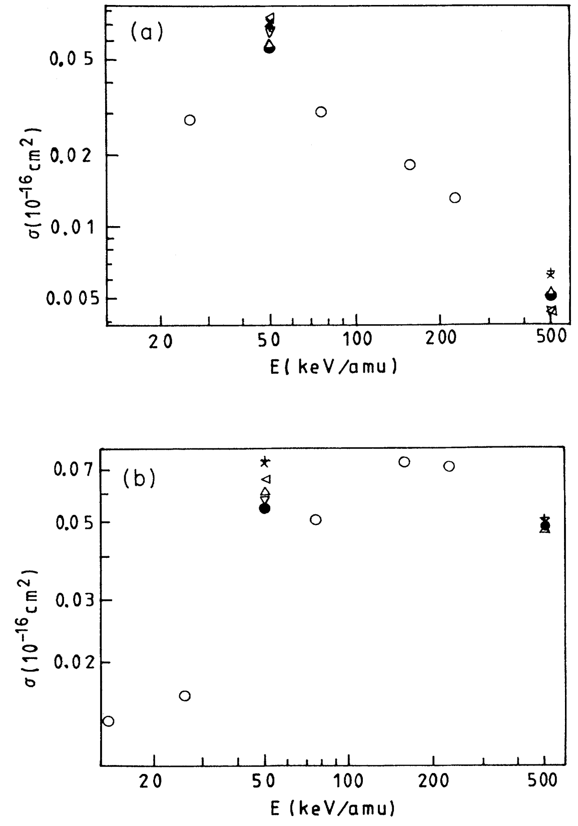

FIG. 8. Excitation cross sections for $He^+(1s)+H^+$ collisions into (a) $He^+(2s)$; (b) $He^+(2p)$. Symbols as in Fig. 7, except ○, theoretical results of Bransden and Noble [29].

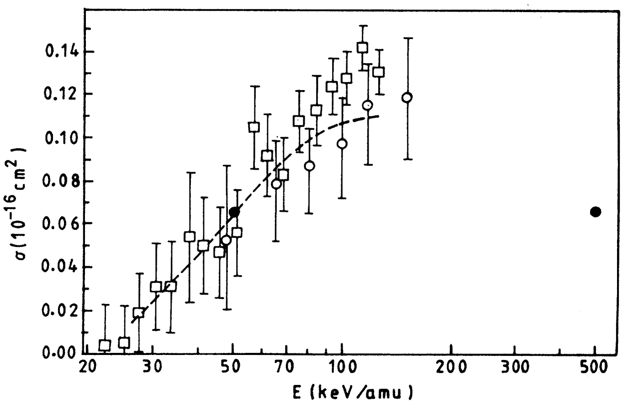

FIG. 9. Ionization cross section for $He^+ + H^+$ collisions. ●, present results obtained from a value of the parameter $\mu = 150$ in Eq. (34) (see discussion in text); — — —, theoretical results of Winter [25]; □, measurements of Rinn *et al.* [26]; ○, measurements of Watts, Dunn, and Gilbody [30].

(ii) Regularization of the Coulomb potential ($\mu \le 5$) permits us to reproduce charge exchange as well as ionization, and yields electron-loss cross sections that are in agreement with experimental values (Fig. 7). In particular, at low energies (e.g., $E = 50$ keV amu^{-1}) where charge exchange dominates ionization, our cross section is close to the corresponding measurement [25]. An optimal regularization for $\mu \simeq 2.5$ is found when there is a close similarity between the shape of the potential (34) near the projectile and the $1s_H$ orbital.

From (i) and (ii), it may be reasoned that if we can separately obtain electron loss and ionization data, by subtracting them we can also evaluate the corresponding values for charge exchange. Indeed, our calculations show that this procedure is accurate even for individual trajectories. As an illustration, we compare in Fig. 10 our values for the charge-exchange probability times the impact parameter b versus b for an impact energy $E = 50$ keV amu^{-1}, together with those of an accurate calculation [31]. Our data were obtained by subtracting the probabilities obtained with the values $\mu = 2.5$ (yielding electron loss) and $\mu = 150$ (yielding target ionization) in (34). For comparison purposes, we also include in the figure our prediction for the ionization probability.

IV. CONCLUSION

Close-coupling techniques often break down when transitions to a continuum (or quasicontinuum) are important. A simple method was recently proposed [10] to offset this difficulty through the augmentation of the close-coupling basis by selected representatives (called absorbers) of the part of functional space not spanned by the original basis. The method has been applied [16,17] in the framework of the molecular treatment of atomic collisions. For different—e.g., atomic—expansions, its implementation is not straightforward because Coulomb potentials introduce divergences in the energies and couplings of the representative functions.

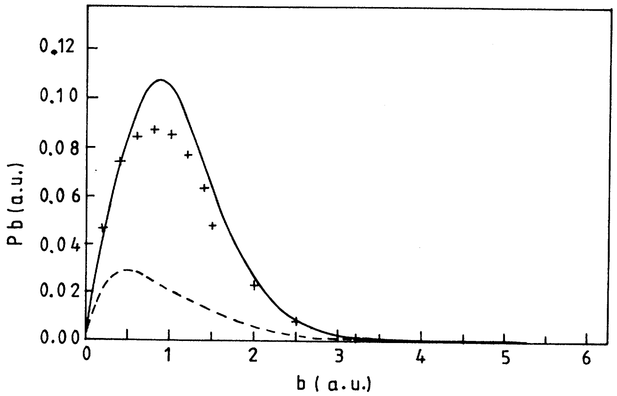

FIG. 10. Probability for charge exchange times the impact parameter b vs b in $He^+ + H^+$ collisions for a nuclear trajectory with $b = 1$ a.u. and an impact energy $E = 50$ KeV/amu ($v = 1.414$ a.u.). ——, present results obtained as explained in text; +, electron-capture results of Winter [31]. For comparison purposes, we also present our prediction (— — —) for the ionization probability, obtained with the potential of (34) with $\mu = 150$ (see text).

In the previous sections we have analyzed the source of those divergences. We have shown, both analytically and numerically, that absorbers have an unphysical character near the Coulomb singularity because they contain contributions from extremely-high-energy states. Since these states are physically inaccessible, their contribution should be eliminated in any meaningful definition.

Our analysis suggests a solution to the problem through a regularization of the Coulomb interactions. We have shown that this solution follows naturally from a more flexible definition of absorber wave functions, which allows the calculation of partial cross sections. The introduction of partial absorbers in the close-coupling expansion may be viewed as a blend of the previous theory [10] and the method of packet states [11–15], and encompasses the treatment of resonant as well as nonresonant transitions. We have further reasoned that nonlocal and local regularization procedures are expected to yield similar results.

Preliminary applications on $H^+ + He^+(1s)$ collisions with a one-center basis and a local regularization (34) of the (projectile) Coulomb potential show that excitation probabilities are independent of regularization; that use of reasonable choices for the regularization parameter yields accurate electron-loss cross sections; and that using both regularized and (quasi) singular potentials allows to calculate separately charge-exchange and ionization cross sections.

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