PHYSICAL REVIEW A **66**, 012710 (2002)

Two-center convergent close-coupling approach to positron-hydrogen collisions

Alisher S. Kadyrov* and Igor Bray†
Centre for Atomic, Molecular and Surface Physics, School of Mathematical and Physical Sciences, Murdoch University, Perth 6150, Australia

(Received 13 February 2002; published 22 July 2002)

The question of convergence in two-center close-coupling expansions is addressed via the study of positron-hydrogen scattering. It is found that the major cross sections do converge if sufficient number of states from a complete basis, centered separately on the hydrogen atom and positronium, are used to expand the total scattering wave function. The underlying equations are computationally highly ill conditioned, and a simple, numerically efficient technique is given that alleviates the problem. Generally, we find good agreement with available experiment and some previous theory. However, calculations that only used eigenstates for the positronium center yielded cross sections for positronium formation in the $2s$ and $2p$ states that are higher than the convergent ones obtained in this work.

DOI: 10.1103/PhysRevA.66.012710 PACS number(s): 34.85.+x

I. INTRODUCTION

The problems of electron- and positron-hydrogen scattering, on the surface, may seem to be very similar. The former has the complexity of exchange arising from the indistinguishability of electrons, while the latter has the complexity of rearrangement due to the formation of positronium (Ps). Formal theory tells us that exchange may be treated as a rearrangement process, yet it turns out that the numerical treatment of electron exchange is much simpler than that of Ps formation. The two problems share similar complexity in the treatment of the target excitation and the three-body continuum. However, the positron scattering problem also has Ps formation and excitation away from the system's center of mass. Thus, the positron scattering system has two (atom and Ps) natural centers whereas the electron scattering system has only one.

The close-coupling method has been very successful in treating electron-atom scattering problems. It has many numerical implementations such as R matrix [1,2], integro-differential close coupling [3], hyperspherical close coupling [4], and momentum-space based convergent close coupling (CCC) [5]. These techniques rely on a sufficiently large single-center expansion of the total wave function in order to correctly take into account the possible atomic excitation and ionization processes. In particular, the CCC method utilizes a complete Laguerre basis for this purpose. The target Hamiltonian is diagonalized in this basis resulting in negative- and positive-energy states. With increasing basis size the negative-energy states converge to true discrete eigenstates, while the positive-energy states provide a more dense discretization of the continuum. Convergence, in the transition of interest, is obtained by simply increasing the basis size.

The same idea can be applied to positron scattering except that now two-center expansions are required. Such expansions readily incorporate the required boundary conditions having bound atomic and Ps channels, but appear to have double counting of the continuum. It is this problem that has attracted our interest in recent times, and we address it here. Thus we are particularly interested in obtaining convergence in calculations of the CC($\bar{N},\bar{N}'$) type, with a basis consisting of N atomic and N' positronium negative- and positive-energy eigenstates and pseudostates. We use a bar on the basis size to indicate the usage of pseudostates, no bar indicates the usage of only true eigenstates.

Two-center close-coupling calculations have been extensively applied in the 1990s [6–9]. Higgins and Burke [7] used the CC(1,1) model across a broad range of energies and found a large and unexpected resonance around 40 eV incident energy. Though a substantial number of papers have been devoted to the study of this resonance, and those found in CC(3,3) calculations [10], these resonances are not real. The first indication of this was shown by Kernoghan *et al.* [11], who suggested that CC($\bar{N},N'$)-type calculations remove these spurious resonances. However, utilizing S-wave model we found that this was not the case [12]. Instead, only calculations of the type CC($\bar{N},\bar{N}'$) showed that this resonance disappears, for relatively small N and N'.

Calculations of the type CC($\bar{N},N'$), where a large number of atomic states were supplemented by a few Ps eigenstates have dominated the literature. An exception to this was the work of Kernoghan *et al.* [13] who used a CC($\bar{9},\bar{9}$) calculation utilizing s-, p-, and d-pseudostates on both centers. Unfortunately, this calculation yielded pseudoresonances associated with a small expansion, and was later superseded by the CC($\bar{30}$,3) calculations which showed smoother results [14]. A similar conclusion was found by Mitroy [15]. Mitroy and Ratnavelu [16] have performed convergence studies using CC($\bar{13},\bar{8}$) calculations for the full positron-hydrogen problem at low energies. Below the ionization threshold they showed good agreement between sufficiently large pseudostate close-coupling calculations and the accurate variational calculations of Humberston [17]. However, at energies above the breakup threshold the situation is less clear, and this is of primary interest to us.

The first extension of the CCC method [18] to the

---

*Electronic address: A.Kadyrov@murdoch.edu.au
†Electronic address: I.Bray@murdoch.edu.au

positron-hydrogen system was without allowance for positronium (Ps) formation [19,20]. It was shown that single-center expansions may yield correct results in certain restricted kinematical regimes, but are generally inadequate. The CCC method has been generalized to incorporate Ps formation channels and be applicable to the *S*-wave model of the positron-hydrogen scattering [12]. For this model we were able to explicitly demonstrate the convergence of the (nonorthogonal) two-center expansions. Moreover, it turns out that the convergence is only possible when two independent large enough Laguerre bases are employed to both of the centers. Most noteworthy is that the cross section for the total breakup of the system into three free particles has two independently converged contributions: ionization of the hydrogen atom and electron capture to the Ps continuum. Thus, no overcompleteness problems, intuitively associated with nonorthogonal two-center expansions, have been found, even in the three-body breakup channel. However, extreme ill conditioning of the underlying linear equations was encountered as the basis sizes increased.

The purpose of the present work is to investigate the question of convergence in nonorthogonal two-center expansions in the case of the full positron-hydrogen scattering problem. This time, convergence for all physical channels of interest needs to be demonstrated not only as a function of the basis size, but also as a function of the angular momentum of the included states.

The plan of the paper is as follows. The CCC formalism for two-center expansions is given in Sec. II. Details of the calculations are given in Sec. III. The results of the calculations will be presented in Sec. IV. Finally, in Sec. V we highlight the main results, draw conclusions, and discuss future directions for the present work.

II. FORMALISM

A. Basic equations

Consider a system of three particles: positron, proton, and electron. Index α (β) will denote a quantum state in the channel where positron (proton) is free and the other two form a bound state, while index e will be used for the channel where all three particles are free. With this notation the total three-body scattering wave function at a total energy E may be written as

$$(H-E)\Psi=0, \tag{1}$$

where

$$H=H_0+v_\alpha+v_\beta+v_e\equiv H_0+v, \tag{2}$$

and where H_0 is the three-free-particle Hamiltonian, and v_i is the Coulomb interaction between particles of pair i ($i=\alpha,\beta,e$).

The most natural way of building the function Ψ with proper boundary conditions would be expanding it in terms of functions of all asymptotic channels, i.e.,

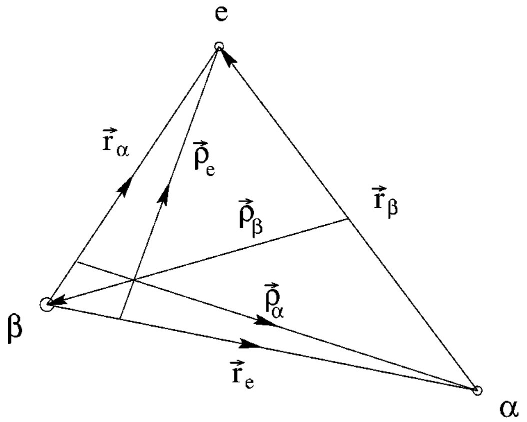

FIG. 1. Jacobi coordinates for a system of three particles: positron (α), proton (β), and electron (e).

$$\Psi\approx\sum_\alpha F_\alpha(\boldsymbol{\rho}_\alpha)\psi_\alpha(\boldsymbol{r}_\alpha)+\sum_\beta F_\beta(\boldsymbol{\rho}_\beta)\psi_\beta(\boldsymbol{r}_\beta)+\int de F_e(\boldsymbol{\rho}_e)\psi_e(\boldsymbol{r}_e), \tag{3}$$

where ψ_α (ψ_β) is a bound-state wave function of atom (Ps) in channel α (β), ψ_e is the regular Coulomb function describing the continuum state of the proton and positron pair, with $F_i(\boldsymbol{\rho}_i)$ being the associated weight function. The Jacobi variable $\boldsymbol{r}_i$ is the relative position of particles in pair i and $\boldsymbol{\rho}_i$ is the position of particle i relative to the center of mass (c.m.) of pair $i(i=\alpha,\beta,e)$. See Fig. 1.

In this work we investigate the possibility of expanding using the full sets of functions (i.e., both bound and continuum) of pairs α and β, thereby representing the effect of states in channel e by continuum states of pairs α and β. Namely,

$$\Psi\approx\left\{\sum_\alpha+\int d\alpha\right\}F_\alpha(\boldsymbol{\rho}_\alpha)\psi_\alpha(\boldsymbol{r}_\alpha)+\left\{\sum_\beta+\int d\beta\right\}F_\beta(\boldsymbol{\rho}_\beta)\psi_\beta(\boldsymbol{r}_\beta). \tag{4}$$

In principle, at this stage we might wish to keep the continuum part only for one of the pairs. However, we found, in practice, that only an expansion of type (4), with the continuum parts for both centers, is capable of giving convergent results in computations [12,21].

The use of true continuum functions is computationally too difficult, and we replace them with Laguerre-based pseudostates, as in electron scattering [18]. Accordingly, Eq. (4) becomes

$$\Psi\approx\sum_\alpha^{N_\alpha}F_\alpha(\boldsymbol{\rho}_\alpha)\psi_\alpha^{(N_\alpha)}(\boldsymbol{r}_\alpha)+\sum_\beta^{N_\beta}F_\beta(\boldsymbol{\rho}_\beta)\psi_\beta^{(N_\beta)}(\boldsymbol{r}_\beta)\equiv\sum_\gamma^{N_\alpha+N_\beta}F_\gamma(\boldsymbol{\rho}_\gamma)\psi_\gamma(\boldsymbol{r}_\gamma), \tag{5}$$

where the index γ ranges over all α and β.

There are a number of ways to find function Ψ in the form (5) to best satisfy Eq. (1). The simplest way consists in using the Bubnov-Galerkin (BG) principle [22] (a scattering analog of the Ritz method widely used in bound state problems in quantum mechanics). We substitute the expansion (5) into Eq. (1) and, according to the BG principle, require that the result be orthogonal to all ($\gamma'=1,\dots,N_\alpha+N_\beta$) basis states

$$\left\langle \psi_{\gamma'} \middle| (H-E)\sum_{\gamma}^{N_\alpha+N_\beta} F_\gamma \psi_\gamma \right\rangle_{\boldsymbol{\rho}_{\gamma'}}=0. \tag{6}$$

In this equation index $\boldsymbol{\rho}_{\gamma'}$ denotes integration over all variables except $\boldsymbol{\rho}_{\gamma'}$, i.e., the result of the integration is a function of $\boldsymbol{\rho}_{\gamma'}$.

The condition imposed above is a system of integro-differential equations for unknown weight functions F_γ. Following [23] we transform these equations for the weight functions to a set of coupled effective two-body Lippmann-Schwinger-type integral equations for transition amplitudes $T_{\gamma'\gamma}$,

$$T_{\gamma'\gamma}(\boldsymbol{q}_{\gamma'},\boldsymbol{q}_\gamma)=V_{\gamma'\gamma}(\boldsymbol{q}_{\gamma'},\boldsymbol{q}_\gamma)+\sum_{\gamma''}^{N_\alpha+N_\beta}\int\frac{d\boldsymbol{q}_{\gamma''}}{(2\pi)^3}\times V_{\gamma'\gamma''}(\boldsymbol{q}_{\gamma'},\boldsymbol{q}_{\gamma''})G_{\gamma''}(q^2_{\gamma''})T_{\gamma''\gamma}(\boldsymbol{q}_{\gamma''},\boldsymbol{q}_\gamma), \tag{7}$$

where $\boldsymbol{q}_\gamma$ is the momentum of free particle γ relative to c.m. of the bound pair in channel γ. The effective two-body free Green's function is defined as

$$G_{\gamma''}(q^2_{\gamma''})=(E+i0-q^2_{\gamma''}/2M_{\gamma''}-\epsilon_{\gamma''})^{-1}, \tag{8}$$

and describes the free relative motion of particle γ'' and bound pair γ'' with binding energy $\epsilon_{\gamma''}$. $M_{\gamma''}$ is the reduced mass of the two fragments in channel γ'' with $M_\alpha=1$ and $M_\beta=2$.

The effective potentials are given by

$$V_{\gamma'\gamma}(\boldsymbol{q}_{\gamma'},\boldsymbol{q}_\gamma)=\langle \boldsymbol{q}_{\gamma'}|\langle\psi_{\gamma'}|U_{\gamma'\gamma}|\psi_\gamma\rangle|\boldsymbol{q}_\gamma\rangle, \tag{9}$$

where

$$U_{\alpha,\alpha}=v-v_\alpha,\quad U_{\beta,\beta}=v-v_\beta,\quad U_{\alpha,\beta}=U_{\beta,\alpha}=H_0+v-E \tag{10}$$

are the potential operators.

Upon partial-wave expansion in total orbital angular momentum J,

$$V_{\gamma'\gamma}(\boldsymbol{q}_{\gamma'},\boldsymbol{q}_\gamma)=\sum_{L',M',L,M,J,K}Y_{L'M'}(\hat{\boldsymbol{q}}_{\gamma'})\times C^{L'l'J}_{M'm'K}\mathcal{V}^{L'L}_{\gamma'\gamma}(q_{\gamma'},q_\gamma)C^{LlJ}_{MmK}Y^*_{LM}(\hat{\boldsymbol{q}}_\gamma), \tag{11}$$

Eq. (7) transforms to (for each J)

$$\mathcal{T}^{L'L}_{\gamma'\gamma}(q_{\gamma'},q_\gamma)=\mathcal{V}^{L'L}_{\gamma'\gamma}(q_{\gamma'},q_\gamma)+\sum_{\gamma''}^{N_\alpha+N_\beta}\sum_{L''}\int\frac{dq_{\gamma''}q^2_{\gamma''}}{(2\pi)^3}\times\mathcal{V}^{L'L''}_{\gamma'\gamma''}(q_{\gamma'},q_{\gamma''})G_{\gamma''}(q^2_{\gamma''})\mathcal{T}^{L''L}_{\gamma''\gamma}(q_{\gamma''},q_\gamma), \tag{12}$$

where L, L' and L'' are the angular momenta of the free particles in channels γ, γ', and γ'', respectively. The effective potentials in the representation of total angular momentum are given by

$$\mathcal{V}^{L'L}_{\gamma'\gamma}(q_{\gamma'},q_\gamma)=\sum_{m',m,M',M}\int\int d\hat{\boldsymbol{q}}_{\gamma'}d\hat{\boldsymbol{q}}_\gamma Y^*_{L'M'}(\hat{\boldsymbol{q}}_{\gamma'})C^{L'l'J}_{M'm'K}\times V_{\gamma'\gamma}(\boldsymbol{q}_{\gamma'},\boldsymbol{q}_\gamma)C^{LlJ}_{MmK}Y_{LM}(\hat{\boldsymbol{q}}_\gamma), \tag{13}$$

where C^{abc}_{def} are the Clebsch-Gordan coefficients of vector addition, $Y_{LM}(\hat{\boldsymbol{q}}_\gamma)$ are the spherical harmonics of unit vector $\hat{\boldsymbol{q}}_\gamma$. The angular momenta of pair γ (γ') are $l(l')$, and M, m, K are the projections of L, l, J, respectively. Accordingly, $K=M+m=M'+m'$.

B. Effective potentials: Direct transitions

Calculation of the effective potentials is straightforward. Consider first the effective potentials for direct transitions (atom-atom or Ps-Ps transitions). For transitions between atomic states we have

$$\begin{aligned}V_{\alpha'\alpha}(\boldsymbol{q}_{\alpha'},\boldsymbol{q}_\alpha)&\equiv\langle\boldsymbol{q}_{\alpha'}|\langle\psi_{\alpha'}|U_{\alpha\alpha}|\psi_\alpha\rangle|\boldsymbol{q}_\alpha\rangle\\&=\int\int d\boldsymbol{\rho}_\alpha d\boldsymbol{r}_\alpha e^{-i\boldsymbol{q}_{\alpha'}\boldsymbol{\rho}_\alpha}\psi^*_{\alpha'}(\boldsymbol{r}_\alpha)\times U_{\alpha\alpha}\psi_\alpha(\boldsymbol{r}_\alpha)e^{i\boldsymbol{q}_\alpha\boldsymbol{\rho}_\alpha}.\end{aligned} \tag{14}$$

Substituting Eq. (14) into Eq. (13) and expanding the plane waves of relative motion yields

$$\mathcal{V}^{L'L}_{\alpha'\alpha}(q_{\alpha'},q_\alpha)=(4\pi)^2 i^{L-L'}\sum_{m',m,M',M}C^{L'l'J}_{M'm'K}C^{LlJ}_{MmK}\times\int\int d\boldsymbol{\rho}_\alpha d\boldsymbol{r}_\alpha\psi^*_{\alpha'}(\boldsymbol{r}_\alpha)U_{\alpha\alpha}\psi_\alpha(\boldsymbol{r}_\alpha)\times j_{L'}(q_{\alpha'}\rho_\alpha)Y^*_{L'M'}(\hat{\boldsymbol{\rho}}_\alpha)j_L(q_\alpha\rho_\alpha)Y_{LM}(\hat{\boldsymbol{\rho}}_\alpha), \tag{15}$$

where the j_L are the spherical Bessel functions.

Using the approximation $\boldsymbol{r}_e\approx\boldsymbol{\rho}_\alpha$ (atomic c.m. assumed to be at the proton) and expanding $U_{\alpha\alpha}=v_e+v_\beta$ in partial waves we get

$$U_{\alpha\alpha}=4\pi\sum_{\lambda\mu}(2\lambda+1)^{-1}\mathcal{U}^\lambda_{\alpha\alpha}(\rho_\alpha,r_\alpha)Y^*_{\lambda\mu}(\hat{\boldsymbol{\rho}}_\alpha)Y_{\lambda\mu}(\hat{\boldsymbol{r}}_\alpha), \tag{16}$$

where

$$\mathcal{U}^{\lambda}_{\alpha\alpha}(\rho_\alpha,r_\alpha)=\begin{cases}\dfrac{\delta_{\lambda 0}}{\rho_\alpha}-\dfrac{\rho_\alpha^{\lambda}}{r_\alpha^{\lambda+1}} & \text{if } \rho_\alpha<r_\alpha,\\[2ex] \dfrac{\delta_{\lambda 0}}{\rho_\alpha}-\dfrac{r_\alpha^{\lambda}}{\rho_\alpha^{\lambda+1}} & \text{otherwise.}\end{cases}\tag{17}$$

It then follows that

$$\begin{aligned}\mathcal{V}^{L'L}_{\alpha'\alpha}(q_{\alpha'},q_\alpha)={}&(4\pi)^{5/2}i^{L-L'}\sum_{m',m,M',M}C^{L'l'J}_{M'm'K}C^{LlJ}_{MmK}\\&\times\int_0^\infty d\rho_\alpha\rho_\alpha^2\int d\boldsymbol{r}_\alpha\psi^*_{\alpha'}(\boldsymbol{r}_\alpha)\psi_\alpha(\boldsymbol{r}_\alpha)\\&\times j_{L'}(q_{\alpha'}\rho_\alpha)j_L(q_\alpha\rho_\alpha)\sum_{\lambda}{}^{(2)}\frac{[L']}{[L\lambda]}\\&\times C^{L'\lambda L}_{M'\mu M}C^{L'\lambda L}_{000}\mathcal{U}^{\lambda}_{\alpha\alpha}(\rho_\alpha,r_\alpha)Y_{\lambda\mu}(\hat{\boldsymbol{r}}_\alpha),\end{aligned}\tag{18}$$

where $[l]=\sqrt{2l+1}$ and $\mu=M-M'$. We take the configuration-space bound-state wave function in form $\psi_\alpha(\boldsymbol{r}_\alpha)=i^l R_{nl}(r_\alpha)Y_{lm}(\hat{\boldsymbol{r}}_\alpha)$, with $R_{nl}(r_\alpha)$ being the square-integrable radial part. Then

$$\begin{aligned}\mathcal{V}^{L'L}_{\alpha'\alpha}(q_{\alpha'},q_\alpha)={}&(4\pi)^2 i^{L-L'+l-l'}\sum_{m',m,M',M}C^{L'l'J}_{M'm'K}C^{LlJ}_{MmK}\\&\times\sum_{\lambda}{}^{(2)}\frac{[L']}{[L]}C^{L'\lambda L}_{M'\mu M}C^{L'\lambda L}_{000}\frac{[l]}{[l']}\\&\times C^{l\lambda l'}_{m\mu m'}C^{l\lambda l'}_{000}I^{\lambda}_{\alpha'\alpha}(q_{\alpha'},q_\alpha),\end{aligned}\tag{19}$$

where all radial information is contained in the integral

$$\begin{aligned}I^{\lambda}_{\alpha'\alpha}(q_{\alpha'},q_\alpha)={}&\int_0^\infty d\rho_\alpha\rho_\alpha^2 j_{L'}(q_{\alpha'}\rho_\alpha)j_L(q_\alpha\rho_\alpha)\\&\times\int_0^\infty dr_\alpha r_\alpha^2 R_{n'l'}(r_\alpha)\mathcal{U}^{\lambda}_{\alpha\alpha}(\rho_\alpha,r_\alpha)R_{nl}(r_\alpha).\end{aligned}\tag{20}$$

Summing over the angular-momenta projections one finally arrives at

$$\begin{aligned}\mathcal{V}^{L'L}_{\alpha'\alpha}(q_{\alpha'},q_\alpha)={}&(4\pi)^2(-1)^{J+(L'+L+l'+l)/2}[L'l]\\&\times\sum_{\lambda}{}^{(2)}C^{L'\lambda L}_{000}C^{l\lambda l'}_{000}\begin{Bmatrix}L' & \lambda & L\\ l & J & l'\end{Bmatrix}\\&\times I^{\lambda}_{\alpha'\alpha}(q_{\alpha'},q_\alpha),\end{aligned}\tag{21}$$

where the braces denote a $6j$ symbol. Step 2 of the sum points to the fact that only the terms corresponding to λ of the same parity as the one of $l'+l$ (or, identically, of $L'+L$) survive.

Effective potentials for $\beta\to\beta'$ transitions (Ps-Ps) are defined as

$$\begin{aligned}V_{\beta'\beta}(\boldsymbol{q}_{\beta'},\boldsymbol{q}_\beta)&\equiv\langle\boldsymbol{q}_{\beta'}|\langle\psi_{\beta'}|U_{\beta\beta}|\psi_\beta\rangle|\boldsymbol{q}_\beta\rangle\\&=\int\int d\boldsymbol{\rho}_\beta d\boldsymbol{r}_\beta e^{-i\boldsymbol{q}_{\beta'}\boldsymbol{\rho}_\beta}\psi^*_{\beta'}(\boldsymbol{r}_\beta)\\&\quad\times U_{\beta\beta}\psi_\beta(\boldsymbol{r}_\beta)e^{i\boldsymbol{q}_\beta\boldsymbol{\rho}_\beta}.\end{aligned}\tag{22}$$

Repeating the above procedure we get for $\mathcal{V}^{L'L}_{\beta'\beta}(q_{\beta'},q_\beta)$ exactly the same expression as Eq. (21) but with $\mathcal{U}^{\lambda}_{\beta\beta}(\rho_\beta,r_\beta)$ in Eq. (20) for $I^{\lambda}_{\beta'\beta}(q_{\beta'},q_\beta)$ defined as

$$\mathcal{U}^{\lambda}_{\beta\beta}(\rho_\beta,r_\beta)=[1-(-1)^{\lambda}]\times\begin{cases}\dfrac{2^{\lambda+1}\rho_\beta^{\lambda}}{r_\beta^{\lambda+1}} & \text{if } \rho_\beta<r_\beta/2,\\[2ex] \dfrac{r_\beta^{\lambda}}{2^{\lambda}\rho_\beta^{\lambda+1}} & \text{otherwise,}\end{cases}\tag{23}$$

since

$$U_{\beta\beta}\equiv\frac{1}{r_e}-\frac{1}{r_\alpha}=\frac{1}{|\boldsymbol{\rho}_\beta+\boldsymbol{r}_\beta/2|}-\frac{1}{|\boldsymbol{\rho}_\beta-\boldsymbol{r}_\beta/2|}.\tag{24}$$

We note that, in general, further reduction of I^{λ} for eigenstates or Laguerre-based pseudostates is possible. However, caution must be exercised as this may lead to an analytical expression more difficult to calculate than a direct numerical integration of Eq. (20). At the same time a numerical calculation of I^{λ} is quite simple since it can effectively be represented as a product of two one-dimensional integrals.

C. Effective potentials: Rearrangement

Calculation of the effective potentials for the rearrangement (atom-Ps) transitions is relatively more involved. The history of such calculations goes back to Massey and Mohr [24]. However, until early 1990s the matrix elements for the general case were not available. Hewitt *et al.* [6] for the first time communicated their results for transition amplitudes between arbitrary hydrogen and positronium states. They calculated the positronium formation matrix elements using the Gaussian representation for the wave functions and the interaction potentials. This work enabled a major breakthrough, when Mitroy [8] calculated the amplitudes in a more general form and in a straightforward manner without the use of additional expansions. Here we follow Mitroy [8]. However, we further reduce the matrix elements analytically calculating pseudostates and form factors in momentum space.

For the purpose of calculation it is convenient to do the following transformation: $\boldsymbol{\rho}_\beta\to-\boldsymbol{\rho}_\beta$ and $\boldsymbol{q}_\beta\to-\boldsymbol{q}_\beta$. Thus now in channel β vector $\boldsymbol{\rho}_\beta$ is the position, and $\boldsymbol{q}_\beta$ is the momentum, of positronium relative to proton. With this transformation the effective potentials for rearrangement $\alpha\to\beta$ transitions are defined as

$$V_{\beta\alpha}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)\equiv\langle\boldsymbol{q}_\beta|\langle\psi_\beta|U_{\beta\alpha}|\psi_\alpha\rangle|\boldsymbol{q}_\alpha\rangle = \int\int d\boldsymbol{\rho}_\beta d\boldsymbol{r}_\beta e^{-i\boldsymbol{q}_\beta\boldsymbol{\rho}_\beta}\psi_\beta^*(\boldsymbol{r}_\beta)(H_0+v_\alpha+v_\beta + v_e - E)\psi_\alpha(\boldsymbol{r}_\alpha)e^{i\boldsymbol{q}_\alpha\boldsymbol{\rho}_\alpha}. \tag{25}$$

Hamiltonian H_0 can be taken in variables of either channel α or β,

$$q_\alpha^2/2+p_\alpha^2/2\equiv q_\beta^2/4+p_\beta^2, \tag{26}$$

where $\boldsymbol{p}_\gamma$ is the momentum of the internal relative motion of the particles of pair γ, a canonical conjugate of the Jacobi variable $\boldsymbol{r}_\gamma$,

$$\boldsymbol{p}_\beta=\boldsymbol{q}_\beta/2-\boldsymbol{q}_\alpha \quad\text{and}\quad \boldsymbol{p}_\alpha=\boldsymbol{q}_\beta-\boldsymbol{q}_\alpha. \tag{27}$$

Split Eq. (25) into two parts,

$$\begin{aligned}V_{\beta\alpha}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)=&\int\int d\boldsymbol{\rho}_\beta d\boldsymbol{r}_\beta e^{-i\boldsymbol{q}_\beta\boldsymbol{\rho}_\beta}\psi_\beta^*(\boldsymbol{r}_\beta)\\ &\times[\mathcal{E}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)+v_\alpha+v_\beta]\psi_\alpha(\boldsymbol{r}_\alpha)e^{i\boldsymbol{q}_\alpha\boldsymbol{\rho}_\alpha}\\ &+\int\int d\boldsymbol{\rho}_\beta d\boldsymbol{r}_\beta e^{-i\boldsymbol{q}_\beta\boldsymbol{\rho}_\beta}\psi_\beta^*(\boldsymbol{r}_\beta)v_e\psi_\alpha(\boldsymbol{r}_\alpha)e^{i\boldsymbol{q}_\alpha\boldsymbol{\rho}_\alpha}\\ \equiv& V_{\beta\alpha}^{(I)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)+V_{\beta\alpha}^{(II)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha),\end{aligned} \tag{28}$$

with $\mathcal{E}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)=q_\alpha^2/2+p_\alpha^2/2-E\equiv q_\beta^2/4+p_\beta^2-E$. Then the parts can be written as

$$\begin{aligned}V_{\beta\alpha}^{(I)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)=&\,\mathcal{E}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)\tilde{\psi}_\beta^*(\boldsymbol{p}_\beta)\tilde{\psi}_\alpha(\boldsymbol{p}_\alpha)+\tilde{\psi}_\beta^*(\boldsymbol{p}_\beta)\tilde{g}_\alpha(\boldsymbol{p}_\alpha)\\ &+\tilde{g}_\beta^*(\boldsymbol{p}_\beta)\tilde{\psi}_\alpha(\boldsymbol{p}_\alpha)\end{aligned} \tag{29}$$

and

$$V_{\beta\alpha}^{(II)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)=\int\frac{d\boldsymbol{q}}{(2\pi)^3}\tilde{\psi}_\beta^*(\boldsymbol{p}'_\beta)\frac{4\pi}{(\boldsymbol{q}-\boldsymbol{q}_\alpha)^2}\tilde{\psi}_\alpha(\boldsymbol{p}'_\alpha), \tag{30}$$

where $\tilde{\psi}(\boldsymbol{p})$ are pseudostate wave functions in momentum space, $\tilde{g}(\boldsymbol{p})$ are pseudo-bound-state form factors (we will call them simply pseudo-form-factors). Here $\boldsymbol{p}'_\alpha$ and $\boldsymbol{p}'_\beta$ are the momenta of relative motion of the particles of the corresponding pairs immediately before and after the actual rearrangement via the Coulomb potential $4\pi/(\boldsymbol{q}-\boldsymbol{q}_\alpha)^2$,

$$\boldsymbol{p}'_\beta=\boldsymbol{q}_\beta/2-\boldsymbol{q} \quad\text{and}\quad \boldsymbol{p}'_\alpha=\boldsymbol{q}_\beta-\boldsymbol{q}, \tag{31}$$

where $\boldsymbol{q}$ is the momentum of the relative motion of fragments in virtual channel e.

First, we transform $V_{\beta\alpha}^{(I)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)$ into the representation of total angular momentum J, then separate the radial parts of the momentum-space pseudostates and pseudo-form-factors according to $\tilde{\psi}_\alpha(\boldsymbol{p})=\tilde{R}_{nl}(p)Y_{lm}(\hat{\boldsymbol{p}})$ and $\tilde{g}_\alpha(\boldsymbol{p})=\tilde{u}_{nl}(p)Y_{lm}(\hat{\boldsymbol{p}})$. Radial parts $\tilde{R}_{nl}(p)$ and $\tilde{u}_{nl}(p)$ will be calculated in the following section. Then

$$\begin{aligned}\mathcal{V}_{\beta\alpha}^{L'L(I)}(q_\beta,q_\alpha)=&\sum_{m',m,M',M}C_{M'm'K}^{L'l'J}C_{MmK}^{LlJ}\int\int d\hat{\boldsymbol{q}}_\beta d\hat{\boldsymbol{q}}_\alpha\\ &\times Y_{L'M'}^*(\hat{\boldsymbol{q}}_\beta)Y_{LM}(\hat{\boldsymbol{q}}_\alpha)Y_{l'm'}^*(\hat{\boldsymbol{p}}_\beta)Y_{lm}(\hat{\boldsymbol{p}}_\alpha)\\ &\times[\mathcal{E}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)\tilde{R}_{n'l'}^*(p_\beta)\tilde{R}_{nl}(p_\alpha)\\ &+\tilde{R}_{n'l'}^*(p_\beta)\tilde{u}_{nl}(p_\alpha)+\tilde{u}_{n'l'}^*(p_\beta)\tilde{R}_{nl}(p_\alpha)].\end{aligned} \tag{32}$$

Decomposing the spherical harmonics of the direction of the relative motion in pairs α and β one gets

$$\begin{aligned}\mathcal{V}_{\beta\alpha}^{L'L(I)}(q_\beta,q_\alpha)=&\,4\pi\sum_{m',m,M',M}C_{M'm'K}^{L'l'J}C_{MmK}^{LlJ}\sum_{l'_1,m'_1,m'_2}C_{m'_1m'_2m'}^{l'_1l'_2l'}\frac{[l'!]}{[l'_1!l'_2!]}q_\beta^{l'_1}(-q_\alpha)^{l'_2}2^{-l'_1}\sum_{l_1,m_1,m_2}C_{-m_1-m_2m}^{l_1l_2l}\frac{[l!]}{[l_1!l_2!]}\\ &\times q_\beta^{l_1}(-q_\alpha)^{l_2}\int\int d\hat{\boldsymbol{q}}_\beta d\hat{\boldsymbol{q}}_\alpha F^{(I)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)Y_{L'M'}^*(\hat{\boldsymbol{q}}_\beta)Y_{LM}(\hat{\boldsymbol{q}}_\alpha)Y_{l_1-m_1}(\hat{\boldsymbol{q}}_\beta)Y_{l'_1m'_1}^*(\hat{\boldsymbol{q}}_\beta)Y_{l_2-m_2}(\hat{\boldsymbol{q}}_\alpha)Y_{l'_2m'_2}^*(\hat{\boldsymbol{q}}_\alpha).\end{aligned} \tag{33}$$

Here

$$F^{(I)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)=\mathcal{E}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)\frac{\tilde{R}_{n'l'}^*(p_\beta)\tilde{R}_{nl}(p_\alpha)}{p_\beta^{l'}p_\alpha^{l}}+\frac{\tilde{R}_{n'l'}^*(p_\beta)\tilde{u}_{nl}(p_\alpha)}{p_\beta^{l'}p_\alpha^{l}}+\frac{\tilde{u}_{n'l'}^*(p_\beta)\tilde{R}_{nl}(p_\alpha)}{p_\beta^{l'}p_\alpha^{l}}, \tag{34}$$

$[l!]=\sqrt{(2l+1)!}$, $l'_1+l'_2=l'$, and $l_1+l_2=l$. Composing two spherical harmonics of the same relative motion in channels α and β we get

$$\mathcal{V}_{\beta\alpha}^{L'L(I)}(q_\beta,q_\alpha)=\sum_{m',m,M',M}C_{M'm'K}^{L'l'J}C_{MmK}^{LlJ}\sum_{l_1',m_1',m_2'}C_{m_1'm_2'm'}^{l_1'l_2'l'}\frac{[l'!]}{[l_1'!l_2'!]}q_\beta^{l_1'}(-q_\alpha)^{l_2'}2^{-l_1'}\sum_{l_1,m_1,m_2}C_{-m_1-m_2m}^{l_1l_2l}\frac{[l!]}{[l_1!l_2!]}$$
$$\times q_\beta^{l_1}(-q_\alpha)^{l_2}\sum_{l_1'',m_1''}{}^{(2)}\,C_{m_1m_1'm_1''}^{l_1l_1'l_1''}C_{000}^{l_1l_1'l_1''}\frac{[l_1l_1']}{[l_1'']}\sum_{l_2'',m_2''}{}^{(2)}\,C_{-m_2-m_2'm_2''}^{l_2l_2'l_2''}C_{000}^{l_2l_2'l_2''}\frac{[l_2l_2']}{[l_2'']}(-1)^{m_2'-m_1}$$
$$\times\int\int d\hat{\boldsymbol{q}}_\beta d\hat{\boldsymbol{q}}_\alpha F^{(I)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)Y_{L'M'}^{*}(\hat{\boldsymbol{q}}_\beta)Y_{LM}(\hat{\boldsymbol{q}}_\alpha)Y_{l_1''m_1''}^{*}(\hat{\boldsymbol{q}}_\beta)Y_{l_2''m_2''}(\hat{\boldsymbol{q}}_\alpha). \tag{35}$$

Now we expand $F^{(I)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)$,

$$F^{(I)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)=2\pi\sum_{\lambda,\mu}\mathcal{F}_\lambda^{(I)}(q_\beta,q_\alpha)Y_{\lambda\mu}^{*}(\hat{\boldsymbol{q}}_\beta)Y_{\lambda\mu}(\hat{\boldsymbol{q}}_\alpha), \tag{36}$$

where the expansion coefficients are given by

$$\mathcal{F}_\lambda^{(I)}(q_\beta,q_\alpha)=\int_{-1}^{1}dzF^{(I)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)P_\lambda(z) \tag{37}$$

and $z=\hat{\boldsymbol{q}}_\beta\cdot\hat{\boldsymbol{q}}_\alpha$. Using the latter we arrive at

$$\mathcal{V}_{\beta\alpha}^{L'L(I)}(q_\beta,q_\alpha)=\sum_{l_1'}\frac{[l'!]}{[l_1'!l_2'!]}q_\beta^{l_1'}q_\alpha^{l_2'}2^{-l_1'-1}\sum_{l_1}\frac{[l!]}{[l_1!l_2!]}q_\beta^{l_1}q_\alpha^{l_2}\sum_{l_1''}{}^{(2)}\,C_{000}^{l_1l_1'l_1''}\frac{[l_1l_1']}{[l_1'']}\sum_{l_2''}{}^{(2)}\,C_{000}^{l_2l_2'l_2''}\frac{[l_2l_2']}{[l_2'']}$$
$$\times\sum_{\lambda}{}^{(2)}\,\mathcal{F}_\lambda^{(I)}(q_\beta,q_\alpha)\frac{[L'\lambda]}{[l_1'']}C_{000}^{L'\lambda l_1''}\frac{[L\lambda]}{[l_2'']}C_{000}^{L\lambda l_2''}\sum_{m',m,M',M,m_1',m_1,m_1'',m_2'',\mu}(-1)^{l_2'+l_2+m_2'-m_1+m_1''+m_2''}$$
$$\times C_{M'm'K}^{L'l'J}C_{MmK}^{LlJ}C_{m_1'm_2'm'}^{l_1'l_2'l'}C_{-m_1-m_2m}^{l_1l_2l}C_{m_1m_1'm_1''}^{l_1l_1'l_1''}C_{-m_2-m_2'm_2''}^{l_2l_2'l_2''}C_{M'\mu-m_1''}^{L'\lambda l_1''}C_{M\mu-m_2''}^{L\lambda l_2''}. \tag{38}$$

Summing over all the projections of the angular momenta, which is technically rather involved but straightforward, we finally get

$$\mathcal{V}_{\beta\alpha}^{L'L(I)}(q_\beta,q_\alpha)=[l'lL'Ll'!l!](-1)^{J+L'}\sum_{l_1'}\frac{[l_1'l_2']}{[l_1'!l_2'!]}2^{-l_1'-1}\sum_{l_1}\frac{[l_1l_2]}{[l_1!l_2!]}q_\beta^{l_1'+l_1}q_\alpha^{l_2'+l_2}\sum_{l_1''}{}^{(2)}\,C_{000}^{l_1l_1'l_1''}$$
$$\times\sum_{l_2''}{}^{(2)}\,C_{000}^{l_2l_2'l_2''}\sum_{\lambda}{}^{(2)}\,[\lambda]^2C_{000}^{L'\lambda l_1''}C_{000}^{L\lambda l_2''}\left\{\begin{array}{cccccccc} l_1 & & l & & J & & l' & \\ & l_2 & & L & & L' & & l_1' \\ l_2' & & l_2'' & & \lambda & & l_1'' & \end{array}\right\}\mathcal{F}_\lambda^{(I)}(q_\beta,q_\alpha), \tag{39}$$

where the braces denote the $12j$ symbol of the first kind [25].

Next we transform $V_{\beta\alpha}^{(II)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)$,

$$\mathcal{V}_{\beta\alpha}^{L'L(II)}(q_\beta,q_\alpha)=\sum_{m',m,M',M}C_{M'm'K}^{L'l'J}C_{MmK}^{LlJ}\int\int d\hat{\boldsymbol{q}}_\beta d\hat{\boldsymbol{q}}_\alpha Y_{L'M'}^{*}(\hat{\boldsymbol{q}}_\beta)Y_{LM}(\hat{\boldsymbol{q}}_\alpha)\int\frac{d\boldsymbol{q}}{(2\pi)^3}\tilde{\psi}_\beta^{*}(\boldsymbol{p}_\beta')\frac{4\pi}{(\boldsymbol{q}-\boldsymbol{q}_\alpha)^2}\tilde{\psi}_\alpha(\boldsymbol{p}_\alpha'). \tag{40}$$

Expand the Coulomb potential to get

$$\mathcal{V}_{\beta\alpha}^{L'L(II)}(q_\beta,q_\alpha)=\frac{1}{\pi q_\alpha}\int_0^\infty dqqQ_L\left(\frac{q^2+q_\alpha^2}{2qq_\alpha}\right)\sum_{m',m,M',M}C_{M'm'K}^{L'l'J}C_{MmK}^{LlJ}\int\int d\hat{\boldsymbol{q}}_\beta d\hat{\boldsymbol{q}}Y_{L'M'}^{*}(\hat{\boldsymbol{q}}_\beta)Y_{LM}(\hat{\boldsymbol{q}})\tilde{\psi}_\beta^{*}(\boldsymbol{p}_\beta')\tilde{\psi}_\alpha(\boldsymbol{p}_\alpha'), \tag{41}$$

where $Q_L(x)$ is the Legendre function of the second kind. This shows that remaining is the same as for $\mathcal{V}_{\beta\alpha}^{L'L(I)}(q_\beta,q_\alpha)$. The only difference is that $F^{(II)}(\boldsymbol{q}_\beta,\boldsymbol{q}_\alpha)$ is now given by

$$F^{(II)}(\boldsymbol{q}_\beta,\boldsymbol{q})=\frac{\widetilde{R}^{*}_{n'l'}(p'_\beta)\widetilde{R}_{nl}(p'_\alpha)}{p'^{\,l'}_{\beta}\,p'^{\,l}_{\alpha}}. \tag{42}$$

Finally, combining all results for the effective potentials in the rearrangement transitions we get

$$\mathcal{V}^{L'L}_{\beta\alpha}(q_\beta,q_\alpha)=[l'lL'Ll'!l!](-1)^{J+L'}\sum_{l'_1}\frac{[l'_1l'_2]}{[l'_1!l'_2!]}2^{-l'_1-1}\sum_{l_1}\frac{[l_1l_2]}{[l_1!l_2!]}q_\beta^{l'_1+l_1}\sum_{l''_1}{}^{(2)}\,C^{l_1l'_1l''_1}_{000}\sum_{l''_2}{}^{(2)}\,C^{l_2l'_2l''_2}_{000}\sum_{\lambda}{}^{(2)}\,[\lambda]^2$$
$$\times C^{L'\lambda l''_1}_{000}C^{L\lambda l''_2}_{000}\begin{Bmatrix} l_1 & & l & & J & & l' & \\ & l_2 & & L & & L' & & l'_1 \\ l'_2 & & l''_2 & & \lambda & & l''_1 & \end{Bmatrix} I^{\lambda}_{\beta\alpha}(q_\beta,q_\alpha), \tag{43}$$

where

$$I^{\lambda}_{\beta\alpha}(q_\beta,q_\alpha)=q_\alpha^{l'_2+l_2}\mathcal{F}^{(I)}_{\lambda}(q_\beta,q_\alpha)+\frac{1}{\pi q_\alpha}\int_0^\infty dq\,q^{l'_2+l_2+1}$$
$$\times Q_L\left(\frac{q^2+q_\alpha^2}{2qq_\alpha}\right)\mathcal{F}^{(II)}_{\lambda}(q_\beta,q). \tag{44}$$

D. Pseudostates and pseudoformfactors

In this section we define our pseudostates used in the direct-transition amplitudes and calculate the corresponding momentum-space pseudostates and pseudo-form-factors used in the rearrangement amplitudes. We use the pseudostate expansion for the atom and Ps wave functions

$$R_{nl}(r)=\sum_{k=1}^{N}B^{l}_{nk}\xi_{kl}(r), \tag{45}$$

where the basis $\xi_{kl}(r)$ is made of the orthogonal Laguerre functions

$$\xi_{kl}(r)=N_{kl}(2r/a)^{l+1}e^{-r/a}L^{2l+2}_{k-1}(2r/a), \tag{46}$$

with

$$N_{kl}=\left[\frac{2(k-1)!}{a(2l+1+k)!}\right]^{1/2}. \tag{47}$$

Here $L^{2l+2}_{k-1}(2r/a)$ are the associated Laguerre polynomials. Expansion coefficients B^{l}_{nk} are found by, reformulating the general BG principle for this particular case, diagonalizing the two-particle Hamiltonian of the relevant pair. The result formally does not depend on characteristic falloff radius a, however the rate of convergence does. For this reason it will be chosen on the basis of practical convenience. We will return to the specific choice of parameter a in the following section.

The momentum-space pseudostate wave-functions and pseudo-form-factors can be written as Hankel transforms of the relevant configuration-space functions

$$\widetilde{R}_{nl}(p)=\int_0^\infty dr\,r\,j_l(pr)R_{nl}(r) \tag{48}$$

and

$$\widetilde{u}_{nl}(p)=\int_0^\infty dr\,j_l(pr)R_{nl}(r), \tag{49}$$

respectively. Though these transforms resemble known integrals widely used in quantum mechanics, they are not readily available in standard tables. We calculate them solving a classical momentum distribution problem [26] reformulated for pseudoatoms. Skipping the details we give the final result

$$\widetilde{R}_{nl}(p)=2^{2l+2}a^2l!\frac{(ap)^l}{[(ap)^2+1]^{l+2}}$$
$$\times\sum_{k=1}^{N}B^{l}_{nk}N_{kl}\sum_{m=0}^{k-1}(m+l+1)C^{l+1}_{m}\left[\frac{(ap)^2-1}{(ap)^2+1}\right] \tag{50}$$

and

$$\widetilde{u}_{nl}(p)=2^{2l+1}al!\frac{(ap)^l}{[(ap)^2+1]^{l+1}}\sum_{k=1}^{N}B^{l}_{nk}N_{kl}$$
$$\times\sum_{m=0}^{k-1}C^{l+1}_{m}\left[\frac{(ap)^2-1}{(ap)^2+1}\right], \tag{51}$$

where $C^{l+1}_{m}[x]$ are the Gegenbauer polynomials. Integrals contained in the above transformations are given in the Appendix.

III. DETAILS OF CALCULATIONS

In order to calculate the transition matrix elements we have to solve a system of coupled momentum-space integral equations (12) with the effective potentials given by Eqs. (21) and (43). To avoid complex-number arithmetic we introduce the K-matrix as for electron scattering [18]. This transforms Eq. (12) to the following system of equations for the *K*-matrix amplitudes

$$\mathcal{K}^{L'L}_{\gamma'\gamma}(q_{\gamma'},q_{\gamma})=\mathcal{V}^{L'L}_{\gamma'\gamma}(q_{\gamma'},q_{\gamma})+\sum_{\gamma''}^{N_\alpha+N_\beta}\sum_{L''}\mathrm{P}\int\frac{dq_{\gamma''}q^{2}_{\gamma''}}{(2\pi)^3}\times\frac{\mathcal{V}^{L'L''}_{\gamma'\gamma''}(q_{\gamma'},q_{\gamma''})}{E-q^{2}_{\gamma''}/2M_{\gamma''}-\epsilon_{\gamma''}}\mathcal{K}^{L''L}_{\gamma''\gamma}(q_{\gamma''},q_{\gamma}),$$

$$(\gamma,\gamma'=1,\dots,N_\alpha+N_\beta). \tag{52}$$

For numerical solution of these equations we use standard quadrature rules. The kernel of the equations containing principal value integrals is discretized using a Gauss-Legendre quadrature. The problem of channel-dependent singularities is overcome by using a unique quadrature in each channel containing the singularity. Accuracy of the integral in the sense of the principal value was ensured by using a subquadrature consisting of an even number of Gauss-Legendre points, symmetrically distributed in the immediate vicinity of the singular point. This procedure is similar to the widely used subtraction method with the subtraction being numerically zero.

Fundamentally, the system is highly ill conditioned which makes it impossible to use arbitrarily high basis sizes and quadratures. To alleviate this problem in a numerically efficient fashion we rewrite Eq. (52) in operator form as

$$[I-(1+\delta)\mathcal{V}G]\mathcal{K}(\delta)=\mathcal{V} \tag{53}$$

with the required result obtained for $\delta=0$. Then all derivatives of K with respect to δ have the same form as Eq. (53). In particular, the kernel of the resulting linear equations $I-(1+\delta)VG$ remains the same, only the driving term (right-hand side) changes. This is computationally very important as the majority of the time, required to solve the linear equations, goes on factoring the kernel. Consequently, the associated computer code allows for an arbitrary number of derivatives to be evaluated with almost no extra CPU time or memory being required in practical calculations. Assuming that $K(\delta)$ is analytic in the neighborhood of small δ, we can reconstruct $K(\delta=0)$ from nonzero δ using a Taylor series.

We give an example in Fig. 2 of the behavior of the system for 30 eV incident energy. For speed of calculation at the many values of δ we only included *s* states of both H and Ps. Ten each of H and Ps Laguerre-based states were used with around 100 quadrature points [dq integration in Eq. (52)]. Looking at the reciprocal condition number [27] first, we see that the system of linear equations is ill conditioned, particularly for $|\delta|\approx 0$. To be more specific, when $\delta=0$ we have difficulty in obtaining stable *K*-matrix elements. However, ill conditioning improves rapidly as $|\delta|$ increases away from zero and the results become stable. Examining the analytical behavior of the resulting $K(\delta)$-matrix elements we see an interesting situation. For negative δ the behavior is mostly linear with δ, and consequently an accurate estimate at $\delta=0$ may be obtained using just one derivative. However, for $\delta>0$ there appear to be singularities. Since we solve Eq. (52) along the real axis, these poles should correspond to boundstates and/or resonances. Thus a slight increase in the magnitude of the kernel makes the latter support bound- or weakly bound states above the three-body breakup threshold, which is unphysical. This makes reconstruction of $K(\delta=0)$ using $\delta>0$ impossible. However, decreasing the magnitude of the kernel is harmless. We see that for $\delta<0$ the corrected results are almost perfectly flat, i.e., independent of δ, and hence demonstrate the utility of the present approach. We used $\delta=-0.01$ with one derivative correction for all subsequent calculations.

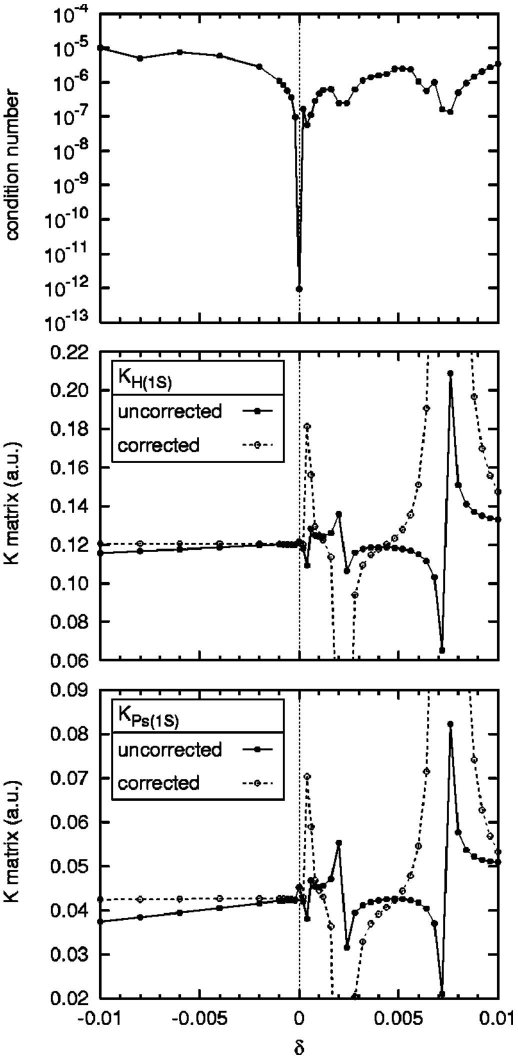

FIG. 2. Reciprocal condition number (top) and *K*-matrix elements as a function of δ, see Eq. (53). The dots indicate the values of δ at which the calculations were performed. The "uncorrected" results are direct solutions of (53). The "corrected" results have used the first derivative $K'(\delta)$, obtained together with $K(\delta)$, to estimate the result at $K(\delta=0)$.

Calculation of the effective potentials for direct transitions, Eq. (21), requires evaluation of the integrals in Eq. (20). The latter can be calculated to a desired accuracy, typically five significant figures in the present work. This is accomplished by integrating out to 400 a.u. on a sufficiently fine radial mesh. The direct-transition potential matrix elements are calculated particularly quickly.

As shown in the preceding section the positronium formation matrix elements have been written as a coupling of 12 actual and virtual angular momenta, leading to finite angular momentum sums and two-dimensional (in the worst case) integrals. Our formulation allows the momentum-space pseudostates and corresponding form factors to be reduced to compact analytical expressions as opposed to highly oscillatory integrals used earlier [8]. To evaluate the integral over the momentum of the virtual electron involving the Coulomb singularity consider a transformation of the integral in Eq. (44) to

$$\int_0^\infty dq f(q) Q_L\left(\frac{q^2+q_\alpha^2}{2qq_\alpha}\right) = \int_0^1 \frac{dt}{t}\left[q_\alpha t f(q_\alpha t)+\frac{q_\alpha}{t} f\left(\frac{q_\alpha}{t}\right)\right] Q_L\left(\frac{t^2+1}{2t}\right). \tag{54}$$

The idea behind this transformation becomes clear if we note that

$$Q_0\left(\frac{t^2+1}{2t}\right)=2Q_0(t)=\ln\frac{t+1}{t-1}, \tag{55}$$

and hence the end-point logarithmic singularity can be used as a weight function to evaluate the integral we need. For this weight function we produce orthonormal Chebyshev polynomials which yield an optimal Gauss-Chebyshev quadrature. For $L>0$ there are no singularities. This approach leads to immense computational savings. The Q_L do not depend on channel information nor the mesh used for solving the integral equations. Thus, the nonsingular part of Q_L (apart from Q_0) can be calculated once, and stored for general use together with the quadrature points and weights corresponding to Q_0. This procedure dramatically speeds up the evaluation of the most time-consuming part of the present calculations. For testing purposes we implemented also the singularity subtraction method which was used by Mitroy [8]. The latter proved to be equally efficient for relatively small calculations and small J. However, its efficiency rapidly diminishes in the case of bigger calculations, involving larger number of channels and partial waves. This fact is a result of the necessity of recalculating Q_L in each channel and for each point of the integral equation mesh, which becomes computationally expensive with increasing L. We took 82 Gauss-Chebyshev quadrature points, sufficient to provide double precision accuracy for the integral (54).

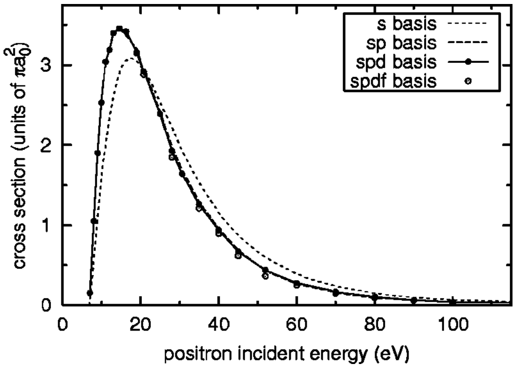

FIG. 4. Total Ps-formation cross section for $e^+ +$ H scattering.

Calculations are performed for a limited number of partial waves J. Extrapolation to infinite J is done using the Born subtraction method for the direct scattering cross sections and a geometric series method for the positronium formation cross sections. A number of test runs at intermediate energies showed that the first ten partial waves were sufficient for reliable extrapolation in the Ps formation channels, while for the same in the direct scattering channels we had to include explicitly 10 more partial waves. The total cross sections are obtained as a sum of all cross sections. The breakup cross section is defined as a sum over the open positive-energy H and Ps pseudostates.

Finally, the generalized CCC computer code has been tested against the CC(3,3) [10], CC($\overline{28}$,3) [15], and CC($\overline{30}$,3) calculations [14]. All were reproduced to a satisfactory accuracy.

IV. RESULTS

One of the main results of our previous work [12] was that widely used CC($\overline{N}$,N') calculations, with atomically based pseudostates and few eigenstates of Ps, were unable to eliminate unphysical resonances. At the same time it was demonstrated that in the case of ($\overline{N}$,$\overline{N}$) bases, i.e., with the

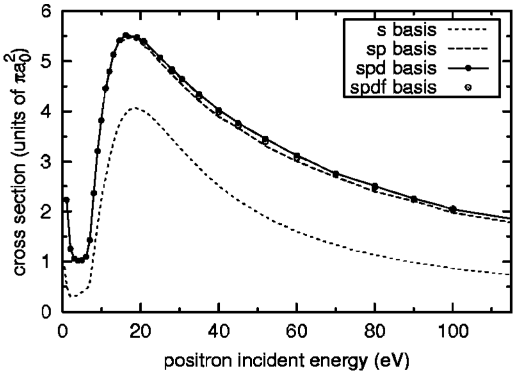

FIG. 3. Total cross section for $e^+ +$ H scattering.

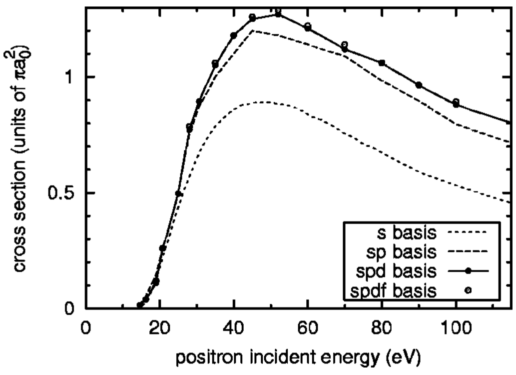

FIG. 5. Total breakup cross section for $e^+ +$ H scattering.

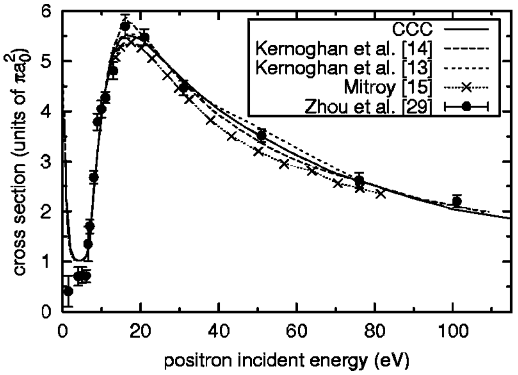

FIG. 6. Total cross section for $e^+ +$ H scattering.

pseudostates around both centers, spurious resonances disappeared quickly for relatively small N. Since the model problem considered in [12] is an important constituent of the full problem, we expect the earlier conclusions to also hold for the full problem.

Now let us consider the full positron-hydrogen problem. Calculations with bases sizes $N=\Sigma_l N_l$ now need to be checked for convergence with orbital angular momentum l, in addition to N_l. Our primary interest is above the ionization threshold, where the cross sections are expected to be smooth as a function of incident energy. For brevity of presentation we take the same number of Laguerre-based states at each incident energy. Any deviation from smooth cross sections indicates the level of convergence with N_l. We set $N_l'=N_l$. This is not necessary, but demonstrates that we are able to treat either center equivalently. We take $N_l=10-l$ with Laguerre exponential falloff parameter being varied slightly around the optimal value for the ground state. The variation is used above the ionization threshold to ensure that the total energy bisects two pseudothresholds [28]. To show convergence with l we give some results from $l\leqslant 1,\ 2$, and 3 calculations. The largest calculations performed had a total of 68 states, 34 each of H and Ps.

We begin with a study of convergence for the total, total Ps formation, and total breakup cross sections, given in Figs. 3–5, respectively. Reasonably smooth cross sections are obtained for all bases with l convergence being rather rapid. For the three cases considered f states contribute only marginally. Having established convergence we next make some comparison of the converged results, which we denote by CCC, with the available experiment and some other calculations.

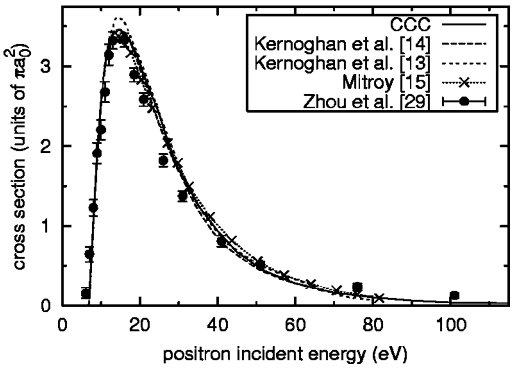

FIG. 7. Total Ps-formation cross section for $e^+ +$ H scattering.

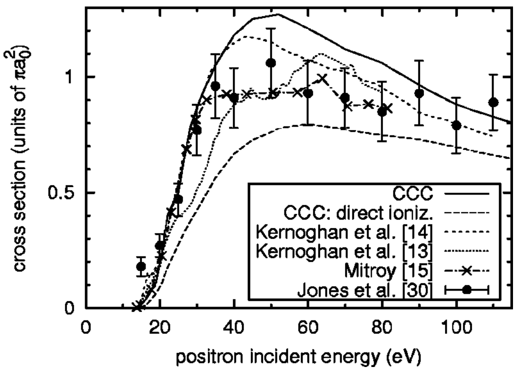

FIG. 8. Total break-up cross section for $e^+ +$ H scattering.

In Figs. 6–8 we compare CCC results with other calculations and experimental data of Zhou *et al.* [29] and Jones *et al.* [30]. Since we are not trying to review the latest calculations we compare our results only with the most relevant close-coupling calculations available on the full energy range. For the status of low-energy variational calculations see Refs. [31] and [32], and references therein. Progress using the Faddeev approach is discussed in Ref. [33]. Results from a coupled-channel optical method may be found in Ref. [34]. As seen from the figures CCC results agree with experiment reasonably well. So do the CC($\overline{9},\overline{9}$) calculations of Kernoghan *et al.* [13], CC($\overline{30}$,3) results of Kernoghan *et al.* [14], and the CC($\overline{28}$,3) data of Mitroy [15]. Note that the CC($\overline{9},\overline{9}$) used an energy averaging procedure to obtain smooth results, whereas the latter two used the n^{-3} scaling rule to estimate the total Ps formation. Such procedures are not necessary in the present work.

What is particularly interesting is that for the case of the break-up cross section the CCC results have two comparable contributions, one from the excitation of the positive-energy H pseudostates (plotted as direct ionization), and the other from excitation of positive-energy Ps pseudostates. A similar result was noted by Kernoghan *et al.* [13] using the CC($\overline{9},\overline{9}$)

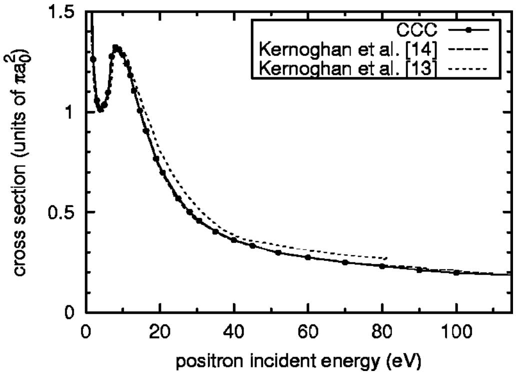

FIG. 9. Elastic cross sections for $e^+ +$ H scattering. The CCC and the calculations of Kernoghan *et al.* [14] are almost indistinguishable.

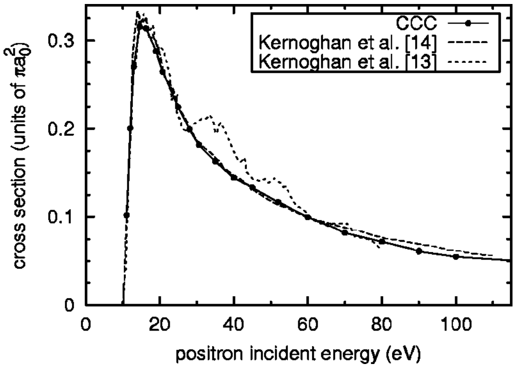

FIG. 10. 2s excitation cross sections for $e^+ +$ H scattering.

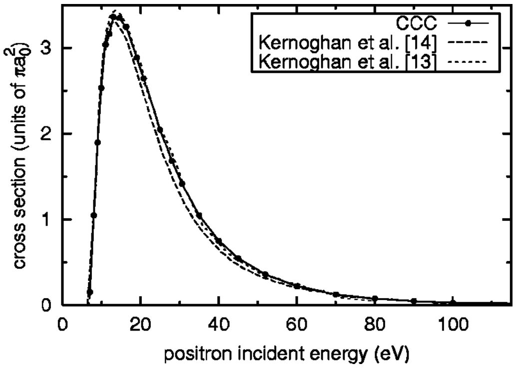

FIG. 12. Cross sections Ps for formation in 1s state in $e^+ +$ H scattering.

calculations. However, for the CC($\overline{N},N'$)-type bases only contribution from direct ionization is possible. At the maximum of the cross section, around 50 eV (same as for electron-impact ionization of H) the separately converged indirect contribution to the break-up cross section is around a third of the total. Yet the CC($\overline{30}$,3) calculations of Kernoghan *et al.* [14] yield only a marginally smaller result. Clearly, absence of Ps positive-energy states is being absorbed by the positive-energy H states. More detailed, differential ionization measurements would be very helpful to test the present formalism.

We next turn to the individual integrated cross sections for scattering of $n \leqslant 2$ states. Beginning with the atomic states, elastic scattering, 2s, and 2p excitation are given in Figs. 9–11, respectively. We see good agreement between the present CCC and the CC($\overline{30}$,3) calculations of Kernoghan *et al.* [14] for the three cases. This indicates that the neglected Ps states have almost no effect on the H cross sections. In Figs. 12–14 the corresponding Ps excitation cross sections are considered. While there is excellent agreement for the excitation of the Ps(1s) state the situation for the Ps(2s) and Ps(2p) states is markedly different. Only the CCC calculation yields relatively smooth results. The CC($\overline{30}$,3) calculation generally substantially overestimates both the 2s and 2p cross sections. The CC($\overline{9}$,$\overline{9}$) calculation of Kernoghan *et al.* [13] shows most oscillation, but is generally closest to the present CCC results. This is not surprising. The CC($\overline{30}$,3) has no allowance for excitation of Ps($n > 2$) states and hence such flux is forced into the Ps($n \leqslant 2$) states. The CC($\overline{9}$,$\overline{9}$) calculation is simply too small to yield convergence.

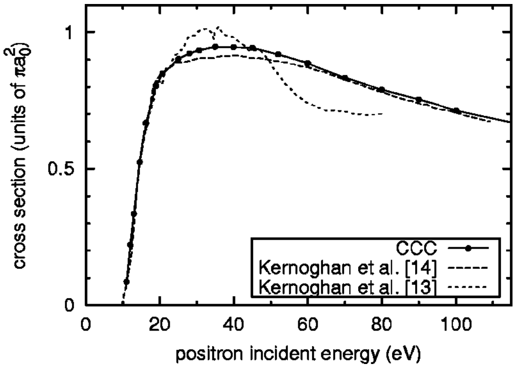

FIG. 11. 2p excitation cross sections for $e^+ +$ H scattering.

V. CONCLUSIONS AND FUTURE DIRECTIONS

Positron-hydrogen scattering problem has been approached according to the full CCC formalism. It has been demonstrated that two-center pseudostate close-coupling approach to the problem may lead to practical convergence. This is possible when large-enough pseudostate expansions are used on both the H and Ps centers. No overcompleteness problems, intuitively associated with nonorthogonal two-center expansions, have been found, even in the three-body breakup channel. However, the underlying equations are highly ill conditioned and numerical techniques are necessary to deal with this issue. The one detailed shows considerable promise not only for positron scattering, but is equally applicable to electron scattering also.

Since in the present CCC approach both centers have been modeled on an equal footing, the principle of detailed balance may be readily applied. Therefore accurate proton-positronium scattering data should be simultaneously calculated and will be a subject of subsequent work. For now we only note that CC($\overline{N},M$) calculations are clearly unable to yield generally accurate results for this problem.

We intend to extend the CCC approach to positron colli-

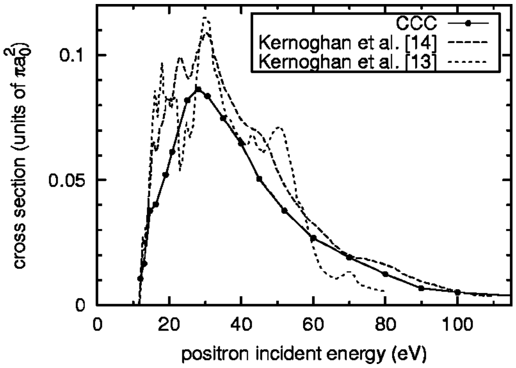

FIG. 13. Cross sections Ps for formation in 2s state in $e^+ +$ H scattering.

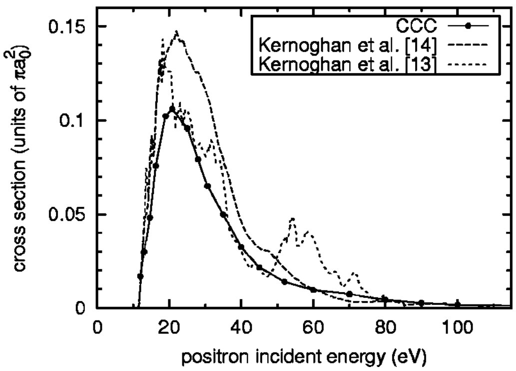

FIG. 14. Cross sections Ps for formation in $2p$ state in $e^+ +$ H scattering.

sions with alkali-metal atoms and helium. So far, theories used either solely eigenstates [35,36] or (above the ionization threshold) an atomically centred L^2 basis, supplemented by a few Ps eigenstates [9]. Results of both approaches systematically underestimate Ps formation cross-section data at low (for alkali-metal atoms) and high (in case of helium) energies. We believe the CCC approach to these problems may cast more light upon the discrepancies between the presently available calculations and measurements.

ACKNOWLEDGMENTS

This work was supported by the Australian Partnership for Advanced Computing. This work was also supported in part by the Maui High Performance Computing Center. Support of the Australian Research Council is gratefully acknowledged.

APPENDIX: USEFUL INTEGRALS

Here we give the Hankel transform integrals calculated in this work, namely,

$$\int_0^\infty dr j_l(pr) r^{l+2} e^{-r/a} L_n^{2l+2}(2r/a) = 2^{l+1} a^{l+3} l! \frac{(ap)^l}{[(ap)^2+1]^{l+2}} \times \sum_{m=0}^{n} (m+l+1) C_m^{l+1}\left[\frac{(ap)^2-1}{(ap)^2+1}\right] \quad \text{(A1)}$$

and

$$\int_0^\infty dr j_l(pr) r^{l+1} e^{-r/a} L_n^{2l+2}(2r/a) = 2^{l} a^{l+2} l! \frac{(ap)^l}{[(ap)^2+1]^{l+1}} \sum_{m=0}^{n} C_m^{l+1}\left[\frac{(ap)^2-1}{(ap)^2+1}\right], \quad \text{(A2)}$$

where $j_l(x)$, $L_n^{2l+2}(x)$, and $C_m^{l+1}[x]$ are the spherical Bessel functions, the associated Laguerre polynomials, and the Gegenbauer polynomials, respectively. The integrals have been obtained for $n,l=0,1,\ldots,$ and $p,a>0$.

---

[1] P. G. Burke and W. D. Robb, Adv. At. Mol. Phys. **11**, 143 (1975).
[2] K. Bartschat, E. T. Hudson, M. P. Scott, P. G. Burke, and V. M. Burke, J. Phys. B **29**, 115 (1996).
[3] W. L. van Wyngaarden and H. R. J. Walters, J. Phys. B **19**, 929 (1986).
[4] D. Kato and S. Watanabe, Phys. Rev. Lett. **74**, 2443 (1995).
[5] I. Bray and A. T. Stelbovics, Adv. At. Mol. Phys. **35**, 209 (1995).
[6] N. R. Hewitt, C. J. Noble, and B. H. Bransden, J. Phys. B **23**, 4185 (1990).
[7] K. Higgins and P. G. Burke, J. Phys. B **24**, L343 (1991).
[8] J. Mitroy, Aust. J. Phys. **46**, 751 (1993).
[9] H. R. J. Walters, A. A. Kernoghan, M. T. McAlinden, and C. P. Campbell, in *Photon and Electron Collisions with Atoms and Molecules*, edited by P. G. Burke and C. J. Joachain (Plenum Press, New York, 1997), pp. 313–345.
[10] K. Ratnavelu, J. Mitroy, and A. T. Stelbovics, J. Phys. B **29**, 2775 (1996).
[11] A. A. Kernoghan, M. T. McAlinden, and H. R. J. Walters, J. Phys. B **27**, L543 (1994).
[12] A. S. Kadyrov and I. Bray, J. Phys. B **33**, L635 (2000).
[13] A. A. Kernoghan, M. T. McAlinden, and H. R. J. Walters, J. Phys. B **28**, 1079 (1995).
[14] A. A. Kernoghan, D. J. R. Robinson, M. T. McAlinden, and H. R. J. Walters, J. Phys. B **29**, 2089 (1996).
[15] J. Mitroy, J. Phys. B **29**, L263 (1996).
[16] J. Mitroy and K. Ratnavelu, J. Phys. B **28**, 287 (1995).
[17] J. W. Humberston, J. Phys. B **17**, 2353 (1984).
[18] I. Bray and A. T. Stelbovics, Phys. Rev. A **46**, 6995 (1992).
[19] I. Bray and A. T. Selbovics, Phys. Rev. A **48**, 4787 (1993).
[20] I. Bray and A. T. Stelbovics, Phys. Rev. A **49**, R2224 (1994).
[21] A. S. Kadyrov and I. Bray, Nucl. Instrum. Methods Phys. Res. B **171**, 119 (2000).
[22] S. G. Mikhlin, *Variational Methods in Mathematical Physics* (Pergamon, Oxford, 1964).
[23] I. H. Sloan and E. J. Moore, J. Phys. B **1**, 414 (1968).
[24] H. S. W. Massey and C. B. O. Mohr, Proc. Phys. Soc., London, Sect. A **67**, 695 (1954).
[25] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum*, 1st ed. (World Scientific, Philadelphia, 1988).
[26] B. Podolsky and L. Pauling, Phys. Rev. **34**, 109 (1929).
[27] E. Anderson *et al.*, *LAPACK* User's Guide (Society for Industrial and Applied Mathematics, Philadelphia, PA, 1992).
[28] I. Bray and B. Clare, Phys. Rev. A **56**, R1694 (1997).
[29] S. Zhou, H. Li, W. E. Kauppila, C. K. Kwan, and T. S. Stein, Phys. Rev. A **55**, 361 (1997).
[30] G. O. Jones, M. Charlton, J. Slevin, G. Laricchia, A. Kövér, M. R. Poulsen, and S. N. Chormaic, J. Phys. B **26**, L483 (1993).

[31] S. Kar and P. Mandal, J. Phys. B **33**, 2379 (2000).
[32] T. T. Gien, J. Phys. B **32**, 2471 (1999).
[33] C.-Y. Hu, D. Caballero, and Z. Hlousek, J. Phys. B **34**, 331 (2001).
[34] M. Z. M. Kamali and K. Ratnavelu, Phys. Rev. A **65**, 014702 (2002).
[35] J. Mitroy and K. Ratnavelu, Aust. J. Phys. **47**, 721 (1994).
[36] G. Ryzhikh and J. Mitroy, J. Phys. B **30**, 5545 (1997).