Elimination of hyperspherical ghost states caused by a closed-shell core: Test with the restricted Temkin-Poet model

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Ghost states arise in applications of the hyperspherical close-coupling method to atoms with two valence electrons outside a closed-shell core. A rigorous formulation of ghost-state elimination is proposed on the basis of a projection operator. Its practical implementation exploits the R-matrix propagator. The procedure is tested for the Temkin-Poet s^2 model by removing a target orbital regarded as an occupied core state. The partial success of the recently proposed scheme of Zhou and Lin [Phys. Rev. A **51**, 1286 (1995)] is accounted for as due to an extreme insensitivity of the R-matrix states on the projection parameter. [S1050-2947(97)01901-X]

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I. INTRODUCTION

Doubly excited states of ideal two-electron systems, such as helium, are often energetically difficult to reach at visible laser wavelengths. Doubly excited states of alkaline-earth-metal atoms, on the other hand, provide easier targets for spectroscopic studies. The initial-state dependence of photoabsorption cross sections [1], the difficulty of selectively exciting intrashell doubly excited states of Ca by two-photon absorption [2], etc., have their intrinsically appealing features for theoretical studies. The study of two-electron correlations in alkaline-earth-metal atoms, as well as their isoelectronic multicharged ions, thus continues to be a subject of spectroscopic and theoretical interest. Different theoretical methods geared to the reproduction of observed spectra have indeed achieved good agreement with the experiment [3]. While the hyperspherical coordinate method proved to be one of the most effective methods when applied to two-electron atoms or ions, the incompatibility of the hyperspherical coordinates and the independent particle coordinates has thus far prohibited successful implementation of the hyperspherical method for the study of two-electron correlations in the valence shell.

Historically, the attempt by Greene [4] to evaluate photoabsorption and ionization cross sections of Be was one of the first to extend the hyperspherical method to systems with a closed-shell core. The general features of the calculated cross sections did have reasonable resemblance to the observed ones, but the quantum defects deviated considerably. At that stage, it was uncertain as to whether the discrepancy originated from some intrinsic fault in the method or from some assumptions on which the analysis was based. An attempt later by Watanabe [5] to calculate the eigenphase shifts for the scattering process $K+e\rightarrow K^{-}{}^{**}\rightarrow K^{*}+e$ yielded a good agreement with the values computed using the standard close-coupling method [6]. So it appears instructive to identify the basic assumptions in the two applications of the hyperspherical method. In both works, a local model potential was employed to represent the potential field of the closed-shell frozen-core electrons. Greene used the standard Hellman-Skillman-type potential that derives from the self-consistent-field (SCF) electronic density. In the hyperspherical method with such a model potential, there appear states that end up occupying the core orbitals, a phenomenon undesirable from the viewpoint of the Pauli exclusion principle. Greene circumvented this phenomenon by eliminating from the calculation of the final-state wave function, the lowest adiabatic channel that converges on the occupied $Be^{+}(1s)$ core asymptotically. Watanabe [5] used instead a pseudopotential proposed in Ref. [7] because it supports no core orbital, the pseudopotential itself being designed to eliminate core orbitals by introducing a repulsive component near the nucleus. This observation concerning the two calculations leads us to suspect that the ghost-state elimination must be done with care. Use of some pseudopotential such as Ref. [7] is probably one of the easiest ways to achieve the elimination. However, there is an undesirable feature in this approach, namely, the fact that the number of nodes of a single-electron wave function turns out equal to the correct number minus the number of the eliminated orbitals. This problem should be resolved in a more rigorous formulation.

In the backdrop of the above-mentioned attempts, Zhou and Lin [8] recently carried out photoionization calculations for Be, employing the SCF-type model potential. However, instead of eliminating the lowest-lying channel throughout the calculations, such as done by Greene, they truncated it only in the asymptotic region of the configuration space. The result agreed very well with experimental as well as other theoretical cross sections. Though the procedure does not seem flawless as it produces deviations at unexpected energy ranges [9], it gives us hopes to represent the correlations of a valence electron pair using the standard SCF model potential. The primary motivation of this paper is to propose a firm theoretical procedure for eliminating ghost states. We will then observe on what accounts the Zhou-Lin procedure produces acceptable results.

Actually, formulating the problem itself is not a difficult task. It requires merely to introduce an appropriate projection operator. Adaptation of the projection operator to the hyperspherical method requires a few more steps. A purpose of this paper is to carry out the adaptation. However, the imple-

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mentation of the procedure for real systems does not seem fruitful at this stage because rigorous convergence checks can be made only with the aid of known analytical solutions. Though such solutions are unavailable in principle, quasianalytical scattering solutions exist for an s^2 configuration model known as the Temkin-Poet model [10,11]. Eliminating a specific core orbital from the model is reasonably straightforward. We will hence test our procedure against the restricted Temkin-Poet model in this paper. Henceforth, we keep this model in mind.

II. THE PROJECTION OPERATOR

Let us denote the core projection operator [12] as

$$P_{\text{core}}=|1s\rangle\langle 1s|. \tag{1}$$

Our aim is to lift by some amount λ the energy of a state which has a $1s$ component in such a way that in the limit of $\lambda\rightarrow\infty$ the state will diminish exponentially. One nontrivial aspect in the application of P_{core} to the current two-electron problem is the representation of its effect on the other electron which may or may not contain a $1s$ component. An answer to this question is simply that the electronic energy be lifted if at least one of the electrons has a $1s$ component. We adopt the following direct product as the two-electron projection operator for its transparent physical meaning,

$$P_{2e}(a,b)=P_{\text{core}}(a)\otimes\underline{1}(b), \tag{2}$$

where $\underline{1}$ is the identity operator and the labels a and b pertain to electron a and electron b for the sake of argument. No symmetrization of this operator is necessary if properly antisymmetrized basis functions are used for evaluating the matrix elements. There may be alternative forms of the two-electron projection operator that can accomplish our purpose. A computationally practical and CPU economic form is desirable, but we will not pursue it here.

Now, we need to adopt a specific representation of the identity operator. Its coordinate representation is the δ function which is numerically awkward to handle. We adopt instead the closure relation,

$$\underline{1}=\sum_k |k\rangle\langle k|, \tag{3}$$

using some complete system $\{|k\rangle\}$. In this work we use as a complete set, functions of the type

$$\langle r|k\rangle=\frac{1}{r}\left(\frac{2}{\Delta}\right)^{1/2}\sin\left(k\pi\frac{r}{\Delta}\right), \tag{4}$$

such that the index k takes on integral values 1,2,3, . . . and $r\in[0,\Delta]$ where Δ represents the upper bound of the domain where the projection operator is effective.

We have now come to an important statement of this section. The Hamiltonian that we deal with is of the form

$$H=H_{2e}+\lambda P_{2e}, \tag{5}$$

where H_{2e} is the standard two-electron Hamiltonian including the model potential with a frozen core. There is no question, in principle, that P_{2e} will indeed serve the purpose as

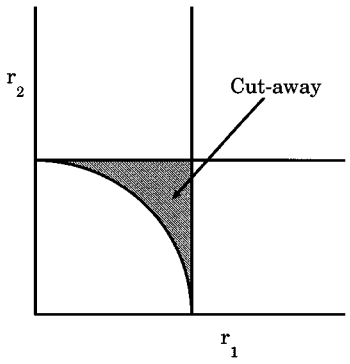

FIG. 1. Domain of integration on the r_1-r_2 plain. The shaded region marked ''cut-away'' is ignored in the evaluation of the projection operator $\tilde{P}_{2e}$. This causes no serious trouble if the domain is large enough to contain the occupied core orbital.

λ eventually goes to $+\infty$. In practice there are a few points we need to pay attention to. First, the domain of integration in evaluating the matrix elements of P_{2e} must be over the entire configuration space. Nonetheless, we need to confine the domain to a finite subspace in practice. This we will indeed do, but as will be seen the restriction does not cause difficulties as long as the domain is large enough to contain the extent of the $1s$ orbital. The complete system for representing the identity operator needs to be thus complete only over the finite domain as specified above. Now, let us realize that the coordinate space realization of P_{2e} is best done using the independent particle radial coordinates $\{r_1,r_2\}$, whereas we employ the hyperspherical coordinates for solving the Schrödinger equation. The relationship between the two sets of coordinates is given by

$$R=\sqrt{r_1^2+r_2^2}, \tag{6}$$

$$\alpha=\tan^{-1}(r_1/r_2), \tag{7}$$

where r_1 and r_2 are the electronic radial distances from the nucleus. The remaining coordinates are defined as usual and denoted simply as Ω. (N.B.: Sometimes Ω is defined as all the variables other than R.) Thus a second point of attention is the short wavelength oscillations associated with higher components of the complete system $\{|k\rangle\}$. Because P_{2e} is defined with respect to a finite domain in the independent particle coordinates, there is a gap between the hyperspherical domain and the square-shaped independent particle domain (see Fig. 1). We will ignore this gap, and evaluate the matrix of P_{core} by integrating over the hyperspherical domain only. The solution is propagated properly, however, by restarting the R-matrix propagator method from the outermost edge of the first sector. This cut-away requires us to check how the short wavelength components contribute to the matrix elements of P_{2e} during an implementation of the present prescription. We will come back to this point in Sec. V.

III. METHOD OF SOLUTION

We divide the process of solving the Schrödinger equation into four steps. The first step sets up the channel functions which we will use for recasting the equation into a

close-coupling type system of ordinary differential equations. The second step solves the close-coupling equations using the R-matrix propagator method. The motivation for employing this method is simply because the projection operator, Eq. (2), is a nonlocal operator. Instead of treating it as an inhomogeneous term in an integrodifferential equation, we prefer to resort to the variational principle directly. The projection operator thus reduces to a matrix. The third step is to propagate the solution further by the R-matrix propagation after the ghost-state elimination is effected. The fourth step of the method is to evaluate an equivalent of the scattering matrix such as the K matrix. However, the gap between the independent particle and hyperspherical coordinates persist in the asymptotic region so that an appropriate matching procedure is required. The established procedure for matching between incompatible coordinates is known as the two-dimensional matching. In this section, we sketch these steps one by one.

A. The hyperspherical adiabatic basis set

The hyperspherical method has been summarized elsewhere [13]. Its successful applications to two-electron atomic systems can be found, for example, in Refs. [14,15], etc. We will therefore outline only the essential ingredients of the method. This subsection, in particular, deals with the adiabatic basis set.

The standard transformation of H_{2e} using the Jacobian $J=\partial(\vec{r}_1,\vec{r}_2)/\partial(R,\alpha,\Omega)=R^5\sin^2\alpha\cos^2\alpha$ results in the reduced two-electron Hamiltonian $\tilde{H}_{2e}=(1/\sqrt{J})H_{2e}(1/\sqrt{J})$ which reads, in atomic units,

$$\tilde{H}_{2e}=\left(-\frac{1}{2}\frac{\partial^2}{\partial R^2}+\frac{H_{ad}}{R^2}\right), \tag{8}$$

where

$$H_{ad}=\frac{1}{2R^2}\left(-\frac{\partial^2}{\partial\alpha^2}-\frac{1}{4}+\frac{\boldsymbol{l}_1^2}{\sin^2\alpha}+\frac{\boldsymbol{l}_2^2}{\cos^2\alpha}+RC(\Omega)\right) \tag{9}$$

is the reduced adiabatic Hamiltonian and $C(\Omega)$, the effective charge, represents the sum of the Coulomb potential terms multiplied by R. Likewise the reduced projection operator reads $\tilde{P}_{2e}=(1/\sqrt{J})P_{2e}(1/\sqrt{J})$. The adiabatic basis set consists of solution vectors $\{\phi_\mu\}$ of the eigenvalue problem

$$H_{ad}\phi_\mu(R;\alpha,\Omega)=U_\mu(R)\phi_\mu(R;\alpha,\Omega). \tag{10}$$

The eigenvalues $U_\mu(R)$ are commonly referred to as adiabatic potential energies as in molecular physics.

We exploit the discrete variable representation (DVR) [16] with Jacobi polynomials as the variational basis, and obtain the eigenvectors $\phi_\mu(R;\alpha,\Omega)$ of Eq. (10) by diagonalizing a symmetric matrix at each R. The procedure assures about six significant digits in the adiabatic basis set throughout. The details about the way the DVR method is extended to solve equations of type (10) with a high precision will be presented in a separate paper.

B. The R-matrix propagator method

Once the adiabatic basis set is constructed, the next step is to solve for the total wave function $\Psi(R,\alpha,\Omega)$ that satisfies

$$\tilde{H}\Psi(R,\alpha,\Omega)=(\tilde{H}_{2e}+\lambda\tilde{P}_{2e})\Psi(R,\alpha,\Omega)=E\Psi(R,\alpha,\Omega). \tag{11}$$

Thus, it is customary to expand the radial coefficients $F_\mu(R)$ in the adiabatic representation, namely,

$$\Psi(R,\alpha,\Omega)=\sum_\mu F_\mu(R)\phi_\mu(R;\alpha,\Omega). \tag{12}$$

This representation, however, requires us to evaluate somewhat cumbersome derivative coupling terms. Instead, Ref. [13] employed the diabatic-by-sector method which defines a locally *diabatic* set out of the adiabatic set by disallowing local variations of R, that is to use the set $\{\phi_\mu(R_{\text{fixed}};\alpha,\Omega)\}$ over a sector surrounding R_{fixed}. Thus the modified form of the expansion is

$$\Psi(R,\alpha,\Omega)=\sum_\mu F_\mu(R)\phi_\mu(R_{\text{fixed}};\alpha,\Omega). \tag{13}$$

Within each sector $F_\mu(R)$ satisfies the close-coupling-type equation with no derivative couplings,

$$\sum_\nu\left(-\frac{1}{2}\frac{\partial^2}{\partial R^2}\delta_{\mu\nu}+\langle\phi_\mu|H_{ad}+\lambda\tilde{P}_{2e}|\phi_\nu\rangle\right)F_\nu(R)=EF_\mu(R), \tag{14}$$

where ϕ_μ and ϕ_ν are all evaluated at $R=R_{\text{fixed}}$. Once the set of solutions are obtained, they may be propagated to the adjacent sector by applying the frame transformation $T^{ij}_{\mu\nu}=(\phi_\mu(R^i_{\text{fixed}};\alpha,\Omega)|\phi_\nu(R^j_{\text{fixed}};\alpha,\Omega))$, that is,

$$\sum_\mu F^i_\mu\left(R^i_{\text{fixed}}+\frac{\Delta^i}{2}\right)T^{ij}_{\mu\nu}=F^j_\nu\left(R^j_{\text{fixed}}-\frac{\Delta^j}{2}\right), \tag{15}$$

where the superscripts i and j pertain to the adjacent sectors spanned by the locally diabatic basis $\phi_\mu(R^i_{\text{fixed}};\alpha,\Omega)$ and $\phi_\mu(R^j_{\text{fixed}};\alpha,\Omega)$, respectively; and Δ^i and Δ^j are the associated sector lengths such that $R^i_{\text{fixed}}+\Delta^i/2=R^j_{\text{fixed}}-\Delta^j/2$. Now we focus on solving Eq. (14) using the R-matrix propagator method.

The R-matrix propagator method was originally conceived by Light and Walker [17], and later some matrix manipulations were improved on by Nesbet [18]. A long write-up of general computer codes is given in Ref. [19]. It is based on the variational principle so that the solution is stable and rapidly convergent. It exploits the Bloch operator defined by

$$L(R^{(1)},R^{(2)})=-\frac{1}{2}[\delta(R-R^{(1)})-\delta(R-R^{(2)})]\frac{\partial}{\partial R}. \tag{16}$$

We merely sketch the procedure and give key expressions needed for numerical implementation [19]. Suppose we use a radial basis set $\{f_p(R)\}$ within a sector $R\in[R^{(1)},R^{(2)}]$ for expanding $F_\mu(R_{\text{fixed}})$ over. The specific radial basis we exploit in this work consists of normalized Legendre polyno-

mials defined over the interval $[R^{(1)},R^{(2)}]$ by a proper rescaling of the argument. Now the R-matrix method defines a set of eigenvectors $\{|q\rangle\}$ for each sector through the eigenvalue problem

$$(\widetilde{H}+L)|q\rangle=\epsilon_q|q\rangle, \tag{17}$$

such that $|q\rangle$ is a superposition of functions of the form $f_p(R)\phi_\mu(R_{\rm fixed};\alpha,\Omega)$. It then follows that the eigenvector $|u\rangle$ of the Schrödinger equation

$$\widetilde{H}|u\rangle=E|u\rangle$$

satisfies

$$(\widetilde{H}+L)|u\rangle=(E+L)|u\rangle.$$

Consequently,

$$|u\rangle=\sum_q \frac{|q\rangle\langle q|L|u\rangle}{\epsilon_q-E}. \tag{18}$$

Thus at each end point, we have

$$\langle 1|u\rangle=-\frac{1}{2}\sum_q\left(\frac{\langle 1|q\rangle\langle q|1\rangle}{\epsilon_q-E}\frac{\partial}{\partial R}\langle 1|u\rangle - \frac{\langle 1|q\rangle\langle q|2\rangle}{\epsilon_q-E}\frac{\partial}{\partial R}\langle 2|u\rangle\right), \tag{19}$$

$$\langle 2|u\rangle=-\frac{1}{2}\sum_q\left(\frac{\langle 2|q\rangle\langle q|1\rangle}{\epsilon_q-E}\frac{\partial}{\partial R}\langle 1|u\rangle - \frac{\langle 2|q\rangle\langle q|2\rangle}{\epsilon_q-E}\frac{\partial}{\partial R}\langle 2|u\rangle\right). \tag{20}$$

Here and below, we use the indexes 1 and 2 as a shorthand notation for the end points $R^{(1)}$ and $R^{(2)}$. We define the propagator $\mathcal{R}$ by

$$\mathcal{R}_{11}=\frac{1}{2}\sum_q\frac{\langle 1|q\rangle\langle q|1\rangle}{\epsilon_q-E},\quad \mathcal{R}_{12}=\frac{1}{2}\sum_q\frac{\langle 1|q\rangle\langle q|2\rangle}{\epsilon_q-E}, \tag{21}$$

$$\mathcal{R}_{21}=\frac{1}{2}\sum_q\frac{\langle 2|q\rangle\langle q|1\rangle}{\epsilon_q-E},\quad \mathcal{R}_{22}=\frac{1}{2}\sum_q\frac{\langle 2|q\rangle\langle q|2\rangle}{\epsilon_q-E}. \tag{22}$$

The R-matrix $\boldsymbol{R}$ is defined at the end points by

$$\langle 1|u\rangle=\boldsymbol{R}(1)\frac{\partial}{\partial R}\langle 1|u\rangle, \tag{23}$$

$$\langle 2|u\rangle=\boldsymbol{R}(2)\frac{\partial}{\partial R}\langle 2|u\rangle. \tag{24}$$

Substituting Eqs. (21) through (24) into Eqs. (19) and (20) and eliminating the derivatives, we get

$$\boldsymbol{R}(2)=\mathcal{R}_{22}-\mathcal{R}_{21}[R(1)+\mathcal{R}_{11}]^{-1}\mathcal{R}_{12}. \tag{25}$$

This formula allows us to propagate the R matrix obtained at one end of the sector to another, and so forth.

It is also possible to construct wave functions using the propagator. Let us define

$$\mathcal{R}(x;1)=\frac{1}{2}\sum_q\frac{\langle x|q\rangle\langle q|1\rangle}{\epsilon_q-E}, \tag{26}$$

$$\mathcal{R}(x;2)=\frac{1}{2}\sum_q\frac{\langle x|q\rangle\langle q|2\rangle}{\epsilon_q-E} \tag{27}$$

at an arbitrary hyperradius $x\in[R_{(1)},R_{(2)}]$. Consequently, it follows from Eq. (18)

$$\langle x|u\rangle=\mathcal{R}(x;2)\frac{\partial}{\partial R}\langle 2|u\rangle-\mathcal{R}(x;1)\frac{\partial}{\partial R}\langle 1|u\rangle. \tag{28}$$

Thus, by setting $x=R^{(2)}$ we can express $\partial/\partial R\langle 2|u\rangle$ as

$$\frac{\partial}{\partial R}\langle 2|u\rangle=\mathcal{R}_{12}^{-1}\left(\langle 1|u\rangle+\mathcal{R}_{11}\frac{\partial}{\partial R}\langle 1|u\rangle\right). \tag{29}$$

Substituting this and using $\partial/\partial R\langle 1|u\rangle=\boldsymbol{R}(1)^{-1}\langle 1|u\rangle$, we get

$$\langle x|u\rangle=\{\mathcal{R}(x;2)\mathcal{R}_{12}^{-1}[\boldsymbol{R}(1)+\mathcal{R}_{11}]-\mathcal{R}(x;1)\}\boldsymbol{R}(1)^{-1}\langle 1|u\rangle. \tag{30}$$

C. Removal of ghost states during propagation

Let us now recall that the evaluation of a matrix element of the nonlocal operator P_{2e} involves an integration over the entire configuration space. However, the following simple argument delineates the action of P_{2e} on the solution of the Schrödinger equation, Eq. (5), thus providing a guideline for restricting the domain of integration. In the region where the hyperradius R is greater than the size of the occupied $1s$ orbital denoted as $\langle r\rangle$, we have

$$R\simeq r_>+\frac{\langle r\rangle^2}{2r_>}. \tag{31}$$

Thus, R roughly coincides with $r_>$. As a consequence, α roughly coincides with r_{1s}/R. The lowest locally diabatic channel function thus coincides with the $1s$ orbital except for the normalization constant. Thus presuming the integration is taken over some local interval at sufficiently large values of R and also using the δ function representation of the identity operator for the outermost electron, we get

$$P_{2e}\sum_\mu F_\mu(R)\phi_\mu(R_{\rm fixed};\alpha,\Omega)\propto\langle r_<|1s\rangle F_{1s}(r_>). \tag{32}$$

It is clear that at the total energy $E<U_{1s}(r_>)+\lambda$, the radial coefficient $F_{1s}(r_>)$ decays as $e^{-\kappa r_>}$ with $\kappa=\sqrt{2|E-U_{1s}(r_>)-\lambda|}$, where $U_{1s}(r_>)\simeq-0.5$ a.u. For sufficiently large values of λ, $F_{1s}(r_>)$ does not propagate to large distances. Thus we are allowed to confine the integration for the matrix element of P_{2e} to a finite domain, such that $\langle r\rangle$ is sufficiently smaller than the linear size of the

domain. We construct the first sector of the R-matrix propagator method to be as large as necessary to satisfy this condition.

If λ is set very large, we may treat the coefficient $F_{1s}(R)$ of the lowest channel as nil from the second sector onward. This truncation is effectively achieved by retaining, out of the entire R matrix $\mathcal{R}$, the residual submatrix $\mathcal{R}^{\rm res}$ defined through

$$\mathcal{R}=\begin{pmatrix} R_{11} & R_{12} & \cdots & R_{1n} \\ R_{21} & & & \\ \vdots & & \mathcal{R}^{\rm res} & \\ R_{n1} & & & \end{pmatrix}. \tag{33}$$

The eliminated component corresponds to the solution that grows up as $e^{\kappa r_>}$. A slightly more accurate transcription, which we use in this work for truncation, makes use of a pair of local WKB-type radial solutions for each channel, and eliminates the solution whose lowest channel component is exponentially growing.

D. Two-dimensional matching and the *K* matrix

The asymptotic form of the open-channel wave function is

$$\mathcal{F}(r_<,r_>)=\left(\frac{2}{\pi k}\right)^{1/2}\sin(kr_>)\widetilde{f}_n(r_<) \tag{34}$$

for the regular solution and

$$\mathcal{G}(r_<,r_>)=-\left(\frac{2}{\pi k}\right)^{1/2}\cos(kr_>)\widetilde{f}_n(r_<) \tag{35}$$

for the irregular one where $\widetilde{f}_n(r)$ is the volume-normalized bound-state wave function of hydrogen. For closed channels, we have

$$\mathcal{F}(r_<,r_>)=\left(\frac{1}{\pi\kappa}\right)^{1/2}e^{\kappa(r_>-r_m)}\widetilde{f}_n(r_<), \tag{36}$$

for the exponentially growing solution, which we eliminate, and

$$\mathcal{G}(r_<,r_>)=\left(\frac{1}{\pi\kappa}\right)^{1/2}e^{-\kappa(r_>-r_m)}\widetilde{f}_n(r_<) \tag{37}$$

for the exponentially decaying one, which we retain, and r_m is set equal to the matching hyper-radius R_m. We seek to recast the internal R-matrix solution given by

$$\Psi=\boldsymbol{R},\quad \frac{\partial\Psi}{\partial R}=1 \tag{38}$$

as

$$\boldsymbol{\Psi}=\boldsymbol{A}(\mathcal{F}-\boldsymbol{K}\mathcal{G}), \tag{39}$$

$$\frac{\partial\boldsymbol{\Psi}}{\partial R}=\boldsymbol{A}\left(\frac{\partial\mathcal{F}}{\partial R}-\boldsymbol{K}\frac{\partial\mathcal{G}}{\partial R}\right), \tag{40}$$

where $\boldsymbol{K}$ is the K matrix and $\boldsymbol{A}$ is the amplitude. Here the matrix notation is used and the indices are all dropped for simplicity. Multiplying both sides by the adiabatic channel function defined at R_m, and integrating with respect to α results in a system of linear algebraic equations. This linear system is easy to solve for $\boldsymbol{K}$.

IV. THE RESTRICTED TEMKIN-POET MODEL

The s^2 configuration model for the electron-hydrogen scattering was first introduced by Temkin [10] and later rigorously investigated by Poet [11]. It permits one to study the general features of electron-impact excitation at impact energies both below and above the ionization potential. It was thus used earlier as a testing ground for general numerical methods [15,20,21]. Let $f_n(r)$ be a volume-normalized hydrogenic bound-state function $\widetilde{f}_n(r)$ *multiplied* by $n^{3/2}$ where n is the principal quantum number, and $f_\epsilon(r)$ an energy-normalized continuum Coulomb wave function at a suitably chosen continuum energy ϵ as in Eqs. (34)–(37). Let us realize that the two-electron wave function $f_n(r_<)e^{\pm ikr_>}$ as well as $f_{\epsilon_i}(r_<)e^{\pm ikr_>}$ defined at the on-shell energy $E=\frac{1}{2}k^2+\epsilon$ satisfy the Schrödinger equation but not the boundary condition at $r_1=r_2$. At the boundary the wave function must have an antinodal line for ^1S and a nodal line for ^3S. The quantities required of the evaluation of the S-matrix stem from the boundary condition, namely,

$$A_{\epsilon\epsilon'}=\int_0^\infty v_\epsilon^{R*}(r,r)v_{\epsilon'}^R(r,r)dr, \tag{41}$$

$$B_{\epsilon\epsilon_0}=\int_0^\infty v_\epsilon^{R*}(r,r)v_{\epsilon_0}^I(r)dr, \tag{42}$$

where ϵ_0 pertains to the energy of the initial target state, ϵ' to that of a final state, and ϵ to an arbitrary state. The function $v_{\epsilon_0}^I$ pertaining to the initial bound target state is given by

$$v_{\epsilon_0}^I(r_<,r_>)=\frac{\partial}{\partial n}e^{-ikr_>}f_n(r_<) \tag{43}$$

for singlet spin states, where $\partial/\partial n=\partial/\partial r_<-\partial/\partial r_>$, and

$$v_{\epsilon_0}^I(r_<,r_>)=e^{-ikr_>}f_n(r_<) \tag{44}$$

for triplet states. The function v_ϵ^R pertaining to the continuum state is given by

$$v_\epsilon^R(r_<,r_>)=\frac{\partial}{\partial n}\,e^{ikr_>}f_\epsilon(r_<) \tag{45}$$

for singlet states and

$$v_\epsilon^R(r_<,r_>)=e^{ikr_>}f_\epsilon(r_<) \tag{46}$$

for triplet states. Moreover, $v_\epsilon^I=v_{\epsilon'}^{R*}$. For closed channels, we have

$$v_\epsilon^R(r_<,r_>)=\frac{\partial}{\partial n}e^{-\kappa r_>}f_\epsilon(r_<) \tag{47}$$

for singlet states and

$$v_{\epsilon}^{R}(r_<,r_>)=e^{-\kappa r_>}f_{\epsilon}(r_<) \tag{48}$$

for triplet states.

The most noteworthy aspect of the model and of Poet's method of solution is that the S matrix can be obtained by solving a simple system of linear equations of the form

$$\sum_{j=1}^{N}\overline{A_{\epsilon_k\epsilon_j}}c_{\epsilon_j\epsilon_0}=B_{\epsilon_k\epsilon_0}, \tag{49}$$

where

$$\overline{A_{\epsilon_k\epsilon_j}}=\sum_i A_{\epsilon_k\epsilon_i}\alpha_{ij} \tag{50}$$

and α_{ij} represents a set of coefficients defined by $\alpha_{ij}=\int\alpha_i(\epsilon)\alpha_j(\epsilon)d\epsilon$, where

$$\alpha_i(\epsilon)=\frac{(\epsilon-\epsilon_0)\cdots(\epsilon-\epsilon_{i-1})(\epsilon-\epsilon_{i+1})\cdots(\epsilon-\epsilon_N)}{(\epsilon_i-\epsilon_0)\cdots(\epsilon_i-\epsilon_{i-1})(\epsilon_i-\epsilon_{i+1})\cdots(\epsilon_i-\epsilon_N)}. \tag{51}$$

The relationship between $c_{\epsilon_j\epsilon_0}$ and the S matrix $S_{\epsilon_j\epsilon_0}$ is simply

$$S_{ij}=-\left(\frac{k_i}{k_j}\right)^{1/2}\left(\frac{n_i}{n_j}\right)^{3/2}c_{ij}. \tag{52}$$

There is no rigorous theorem guaranteeing the convergence of the solution of Eq. (49) to the desired S matrix as a function of the number of basis functions. However, experience shows that the solution is as good as the unitarity of the obtained S matrix. We may exploit this fact as a guideline in applying the Temkin-Poet model. One last side remark before discussing the restricted model concerns the evaluation of the continuum Coulomb wave functions. Poet himself employed the hypergeometric representation so as to express various matrix elements in Eqs. (41) and (42) analytically. Because the expressions involve hypergeometric functions, multiple precision algorithm (using numbers longer than 8 bytes or eventually even longer than 16 bytes) becomes often necessary. Numerically constructed continuum Coulomb wave functions provide the matrix elements more easily. Thus in this work, the matrices in Eqs. (41) and (42) are constructed using numerical Coulomb wave functions.

Now suppose the $1s$ orbital is occupied. The removal of this orbital is obviously accomplished by restricting ourselves to basis functions that exclude $f_{1s}(r_<)e^{\pm ikr_>}$. However, a literal implementation of this idea yields a poor S matrix in the sense its unitarity is unsatisfactory. It becomes thus necessary to introduce pseudostates. For the precision we aim at in a later section, we include a $1s$ pseudotarget state that is orthogonal to $1s$ and has a node like $2s$ and decays as $e^{-r_<}$. It thus appears that the absence of $1s$, which makes the target states incomplete, requires an auxiliary function to represent ''relaxation.'' From here on, let us call this model and the method of solution for the case of the ''occupied'' $1s$ orbital the restricted Temkin-Poet model.

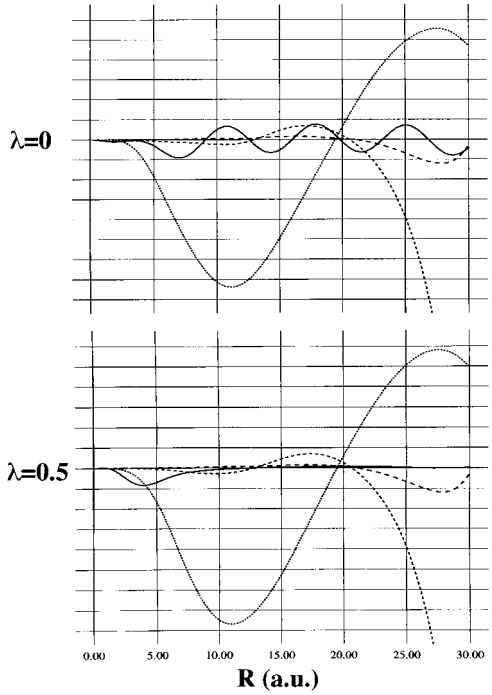

FIG. 2. Channel components of a typical R-matrix solution. The upper panel represents absence of the projection operator, and the lower one is for a relatively small value of $\lambda=0.5$. Using the labels explained in the text, the dominant component represented by the dotted line corresponds to the $2s$ channel, the asymptotically diverging component corresponds to $3s$, the broken line, showing a relatively small amplitude, is for $4s$. The solid line represents the $1s$ channel which has non-negligible amplitude at moderate hyperradial distances. The projection is effected within $R=30$ a.u.

V. RESULT AND DISCUSSIONS

We examine to what extent the procedure outlined in the previous sections results in the final-state wave functions and the S matrix that are physically satisfying. We do so in two steps. First, we visualize the final-state wave functions and observe the way the $1s$ component damps out of the correct solution. Second, we evaluate the S matrix and its associated eigenphase shifts in the energy range from the $2s$ threshold to slightly below the $3s$ threshold. This evaluation will be accompanied by the variation of λ. The number and the quality of the locally diabatic basis set is fixed in such a way as to assure convergence of about three significant digits in the final result. We will examine the Zhou-Lin procedure in parallel.

In the upper panel of Fig. 2, we show the wave function evaluated at $E=-0.12$ a.u. for $\lambda=0$ a.u. This energy lies between the $H(2s)$ and $H(3s)$ thresholds. The size of the first sector is taken to be 30 a.u. Each component $F_{\mu}(R)$ is displayed here with respect to the locally diabatic basis in each sector. It is to be noted that here we use the asymptotic labels $1s, 2s, \ldots$ for μ. The components F_{μ} are evaluated in the *diabatic* representation so that at any finite R these components are formally referenced to the asymptotic channels. The lower panel, on the other hand, is for a relatively small value of $\lambda=0.5$. Each of these wave functions is made to correspond to an R-matrix state in which the derivative of

$\partial F_2(R)/\partial R = 1$ at $R = R_m$, but $\partial F_\mu(R)/\partial R = 0$ for all the other channels. The $\lambda = 0$ case corresponds to the Zhou-Lin prescription. One obvious difference between the two panels is that for $\lambda = 0$ the $\mu = 1s$ component is freely oscillating while for $\lambda = 0.5$ this component rises first, then at R beyond 5 a.u. it decays exponentially. This difference is due to the working of the projection operator, as we so designed. However, *all the other components remain almost uninfluenced by the projection operator*, which is compatible with the surprising finding of Zhou and Lin [8]. An increase in the value of λ leads to a more rapid decay of the $\mu = 1s$ component. Note, however, that an unlimited increase in λ leads to an eventual instability because the radial basis functions used for the R-matrix method become inappropriate to represent the exceedingly sharp exponential decay.

Let us interpret the cause of this weak action of the projection operator on the components other than the $1s$. To this end, it is instructive to consider the system's evolution along R starting from the condensation region where R is small, to the asymptotic region where the residual atomic target states become apparent. The transition region which marks the separation between the two regions varies from state to state, but is generally represented by R close to $\sqrt{2}\langle r\rangle$ where $\langle r\rangle$ is the size of the target state. First, in the condensation region the system does not recognize the presence of the $1s$ state because $r_<(\leqslant R)$ is much smaller than the size of the $1s$ orbital. Hence, the complete adiabatic basis set is necessary for constructing the wave function. It is thus inappropriate to simply exclude the lowest adiabatic channel in this region. Second, the transition region is rather thin. And third, once the system recognizes the $1s$ state on entering the asymptotic region, the residual coupling between the $1s$ state and the rest dies away rapidly. In consequence, in the asymptotic region, the $1s$ component is decoupled from the others so that the boundary condition on this particular component does not influence the component of the other channels. We may also argue for this unexpected success of the Zhou-Lin prescription from a different angle. Suppose we solve the restricted Temkin-Poet model without the pseudostates. We set up the direct product of the $1s$ orbital and the standing-wave solutions, the latter of which are made to vanish beyond some radius r_m. The success of the Zhou-Lin prescription implies a very weak mixing between these standing-wave basis functions and the rest. Consequently, the elastic phase shift reflects very weak dependence on r_m. However, the weak coupling may not hold in the case of eliminating higher core orbitals such as $2s$, $2p$, etc. We will postpone examining such cases. In any event, the truncation of the $1s$ component beyond, say, 7 a.u. appears to provide a reasonable approximation to the projection operator method.

Now we show how our method compares with the S matrix evaluated by the Poet method. The accuracy we attained in this work is about a few percent. We will therefore represent the result only graphically. Figure 3 shows the eigenphase shifts calculated by the Poet procedure and ours. One general tendency is that the Zhou-Lin prescription corresponding to $\lambda = 0$ gives a surprisingly good estimate of δ. With the increase of λ the eigenphase shift approaches that of the restricted Temkin-Poet model. However, it is important to recall our earlier statement that the unlimited increase in λ is undesirable because of the insufficiency of the radial

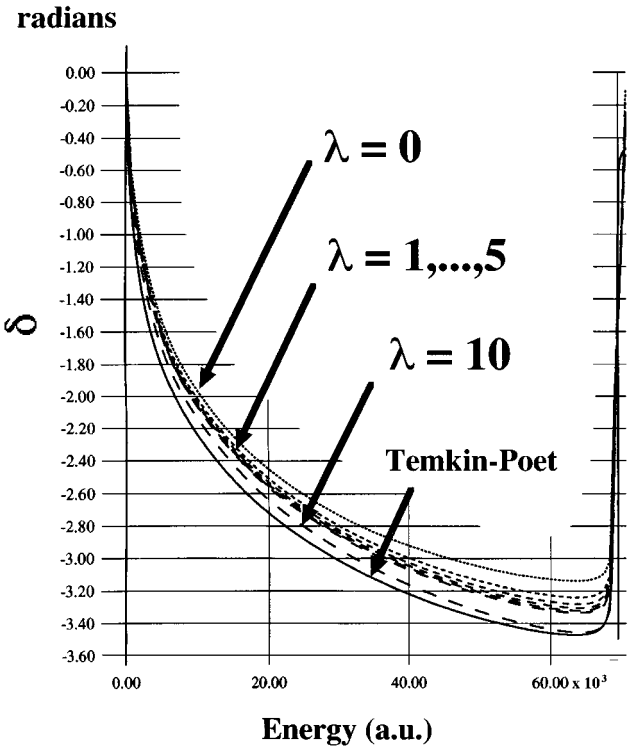

FIG. 3. Elastic eigenphase shift δ shown as a function of energy for different values of λ. $\lambda = 0$ corresponds to the Zhou-Lin prescription, and $\lambda = \infty$ to the restricted Temkin-Poet model. The projection effected within a rather small hyperradius $R = 5$ a.u. which, however, is large enough to contain the $1s$ orbital.

basis functions to represent the sharp exponential decay [12]. There appears to be an optimal value of λ for each set of radial basis functions. In this paper, we do not explore the condition or the prescription that permits us to determine the optimal value of λ for each basis set.

In Sec. II, we made note of a few points of attention. The main effect of cutting the edge off a square block is that the projection operator becomes incomplete in the sense that its eigenvalues are not strictly zero or unity. Instead, the eigenvalues distribute between the two ideal values without a sharp edge. Indeed, the smaller the size of the box is, the more eigenvalues deviate from unity. On the other hand, the good agreement demonstrated in this section suggests that the bad roots play a rather minor role in representing the action of the projection operator.

VI. CONCLUSIONS

With the aid of the restricted Temkin-Poet model, we have shown how to remove an occupied core orbital in the context of the hyperspherical method. Indeed as a function of the parameter λ the elastic eigenphase shift was shown to converge toward the result of the restricted Temkin-Poet model. On the basis of the behavior of the wave function, it was speculated that the remarkable success of the Zhou-Lin prescription for truncating the radial component of the ghost channel owes to the system's rather abrupt recognition of the core $1s$ orbital as well as to the quick decoupling of the

ghost channel from the others in the asymptotic region, or in short, to the weak coupling of the 1s channel with the rest.

The next important step is to redesign the method so as to represent the exponential decay of the ghost channel more effectively. This would permit us to vary the value of λ unrestrictingly and to apply the present approach to real systems.

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