PHYSICAL REVIEW A VOLUME 34, NUMBER 6 DECEMBER 1986

Projection-operator calculations of the lowest e^--He resonance

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(Received 14 July 1986)

Results for the lowest (Schulz) autodetaching state of He$^-$ $[1s(2s)^2]$ are reported. The calculation utilizes the full projection-operator formalism as explicitly developed by Temkin and Bhatia [Phys. Rev. A 31, 1259 (1985)]. Eigenvalues, $\mathscr{E}=\langle\Phi\,|\,QHQ\,|\,\Phi\rangle$, are calculated using projection operators Q depending on increasingly elaborate target wave functions going up to a 10-term Hylleraas-form, and a configuration-interaction total wave function Φ of 40 configurations. Results are well converged, but our best value is $\sim$0.13 eV above the experimental position at 19.37 eV. We conclude that the shift (Δ) in the Feshbach formalism gives a large contribution (relative to the width) to the position E_r $(=\mathscr{E}+\Delta)$. An appendix is devoted to the evaluation of the most complicated type of three-center integral involved in the calculation.

I. INTRODUCTION

Electron resonances can conveniently be studied using the Feshbach formalism.[1,2] Recently, an explicit form of resonant projection operators, P and Q $(=1-P)$, for $(N+1)$-electron systems has been derived.[2,3] In the present paper, these operators are used to calculate the QHQ eigenvalue corresponding to the lowest e^--He resonance, the $1s(2s)^2{:}^2S$ Schulz resonance.[4]

In Sec. II the Rayleigh-Ritz variational calculation of the QHQ eigenvalue spectrum is discussed. Results obtained using five different approximations for the helium target state are reported in Sec. III. In the Appendix, details of the methods used to solve three-electron Hylleraas integrals are presented.

II. VARIATIONAL CALCULATION OF THE *QHQ* EIGENVALUE SPECTRUM

In the projection-operator formalism, the energy of the $1s(2s)^2{:}^2S$ resonance of He$^-$ is the sum of the *lowest QHQ* eigenvalue plus an energy shift arising from the interaction of the QHQ eigenstate with the continuum. In this paper, the Rayleigh-Ritz variational principle is applied to the QHQ eigenvalue problem

$$\delta\left[\frac{\langle\Phi\,|\,QHQ\,|\,\Phi\rangle}{\langle\Phi\,|\,Q\,|\,\Phi\rangle}\right]=0\ . \tag{1}$$

After reviewing the form for the projection operators, P and Q, we shall derive an expression for the action of Q on a three-electron doublet spin eigenstate, $\Phi(^2S)$, i.e., $Q\,|\,\Phi\rangle$. Calculation of the QHQ matrix elements is then discussed.

A. *P* and *Q* operators

We confine ourselves to the $1s(2s)^2{:}^2S$ resonance of He$^-$. The projection operator P has the form[3]

$$P\equiv P_1+P_2+P_3\ , \tag{2}$$

where

$$P_i\equiv P_i(x_1,x_2,x_3) \tag{3a}$$

$$\equiv\psi_0(r^{(i)})\rangle\left[1+\sum_{\alpha}\frac{v_\alpha(r_i)\rangle\langle v_\alpha(r_i)}{\lambda_\alpha-1}\right]\langle\psi_0(r^{(i)})\ ,\qquad i=1,2,3\ . \tag{3b}$$

We use the notation defined in Ref. 3, although some definitions will be repeated here for clarity. $\psi_0(r^{(1)})$ is the channel wave function obtained by coupling the ^1S helium ground state to the angular momentum and spin of an α-spin s-wave electron. For this (^2S) case

$$\psi_0(r^{(1)})=\frac{\alpha(1)}{\sqrt{(4\pi)}}\phi_0(x_2,x_3)\ . \tag{4}$$

The x_i are the totality of coordinates (spin and space) for electron i; $r^{(i)}$ is defined as the collection of coordinates for the $N+1$ electrons with only the radial coordinate of the ith electron, r_i, missing. (Throughout the text integrations in the bras and kets are only over those coordinates which are explicitly arguments of the functions therein.) The helium ground state is the product of a symmetric, normalized spatial function and an antisymmetric, normalized singlet spin function

$$\phi_0(x_2,x_3)=\frac{\alpha(2)\beta(3)-\beta(2)\alpha(3)}{\sqrt{2}}\varphi_0(2,3)\ . \tag{5}$$

The functions $v_\alpha(r)$ and constants λ_α in the above form for P_i, Eq. (3b), are determined from an auxiliary eigenvalue problem which can be reduced to an equivalent but much simpler equation[5]

$$v_\alpha(r_1)=\lambda_\alpha^{1/2}\int_0^\infty f(r_1\,|\,r_2)v_\alpha(r_2)r_2^2dr_2\ , \tag{6}$$

where $f(r_1\,|\,r_2)$ is defined by the equation

$$f(r_1\,|\,r_2)\equiv2\pi\int_{-1}^{1}\varphi_0(r_1,r_2,\theta_{12})d\cos(\theta_{12})\quad(\theta_{12}\equiv\hat{\mathbf{r}}_1\cdot\hat{\mathbf{r}}_2)\ . \tag{7}$$

In this paper the resonance was calculated with a variety of approximate target wave functions, the most sophisticated of which were Hylleraas functions up to degree ω,

$$\varphi_0(1,2)=\sum_{\{l+m+n=0\}}^{\{l+m+n=\omega\}}\frac{C_{lmn}}{(8\pi^2)^{1/2}}r_1^l r_2^m r_{12}^n e^{-\gamma_1 r_1-\gamma_2 r_2}+[r_1\leftrightarrow r_2]\,. \tag{8}$$

The auxiliary eigenvalue equation for the four-term $\{\omega=1\}$ target function has been discussed previously.[5] For arbitrary ω, $f(r_1\,|\,r_2)$ of Eq. (7) is given by

$$f(r_1\,|\,r_2)=\sum_{\{l+m+n=0\}}^{\{\omega\}}\frac{C_{lmn}}{n+2}r_1^{l+1}r_2^{m+1}[(r_1+r_2)^{n+2}-|\,r_1-r_2\,|^{n+2}]\times e^{-\gamma_1 r_1-\gamma_2 r_2}+[r_1\leftrightarrow r_2]\,. \tag{9}$$

The eigenvectors and eigenvalues associated with v_α can be determined from a second variational principle[5]

$$\delta\left[\frac{\langle v_\alpha(r_1)f_\alpha(r_1,r_2)v_\alpha(r_2)\rangle}{\langle v_\alpha(r)v_\alpha(r)\rangle}\right]=0\,. \tag{10}$$

With the expansion (γ_1 and γ_2 being the same as in φ_0)

$$v_\alpha(r)=\sum_{n=0}^{\omega}r^n(d_{1n}^{(\alpha)}e^{-\gamma_1 r}+d_{2n}^{(\alpha)}e^{-\gamma_2 r})\,, \tag{11}$$

for the eigenvectors, the variational principle determines the linear coefficients. Sum rules[5] on the eigenvalues obtained from (11) yield five-place accuracy. Longer expansions were tested and produced little improvement in the sum rules and no appreciable change in final QHQ eigenvalues. Thus, although our solution of (6) is not exact, we can consider it exact for practical purposes.

In nonrelativistic calculations, a spin-free formulation of the eigenvalue problem can be constructed.[6] Let p_1 be a spin-free projection operator

$$p_1=\frac{\varphi_0(2,3)}{\sqrt{(4\pi)}}\Big\rangle\left[1+\sum_\alpha\frac{v_\alpha(r_1)\rangle\langle v_\alpha(r_1)}{\lambda_\alpha-1}\right]\Big\langle\frac{\varphi_0(2,3)}{\sqrt{(4\pi)}}\,, \tag{12}$$

for a three-electron system. Define p_2 and p_3 analogously. We make the following assertion: The action of P on a three-electron doublet spin configuration $|\,\Phi_n\rangle$ is equivalent to the action of $p\equiv p_1+p_2+p_3$ on $|\,\Phi_n\rangle$, i.e.,

$$p\,|\,\Phi_n\rangle=P\,|\,\Phi_n\rangle\,. \tag{13}$$

(The whole wave function $|\,\Phi\rangle$ is understood to be a sum over configurations $|\,\Phi_n\rangle$.) The assertion can be proved by explicitly performing the spin integrations on the right-hand side (rhs) of Eq. (13), and comparing the result to the left-hand side (lhs).

Since P and Q are complementary operators, Q has the form

$$Q=1-(P_1+P_2+P_3)\,. \tag{14}$$

Here, and for the remainder of the text, upper case P's and Q's will be used to denote the spin-free projection operators.

B. Projection $Q\,|\,\Phi_n\rangle$

Let $S(1)$, $U(2)$ and $W(3)$ be one-electron spatial orbitals. In the spin-free formalism, a doublet spin configuration formed by coupling electrons 1 and 3 to a singlet is represented by the sum[6]

$$|\,\Phi_n\rangle=|\,S(1)U(2)W(3)\rangle+|\,W(1)U(2)S(3)\rangle-|\,U(1)S(2)W(3)\rangle-|\,U(1)W(2)S(3)\rangle \tag{15a}$$

$$=[I-(12)][I+(31)]\,|\,S(1)U(2)W(3)\rangle\,. \tag{15b}$$

(Whenever S, U, and W all differ, a second independent doublet eigenstate can be formed by initially coupling electron 2 to either of the other two electrons to form a singlet or by initially coupling two of the electrons to a triplet.) Here the identity operator is I, and $(ijk\cdots n)$ is the permutation operator which takes i into j, j into $k,\ldots,$ and n into i.

Since $\varphi_0(1,2)$ equals $\varphi_0(2,1)$, it is clear that $\langle\varphi_0(1,2)\,|\,[I-(12)]=0$; thus utilizing Eqs. (12) and (15b), it follows that $P_3\,|\,\Phi_n\rangle$ vanishes. This implies $P\,|\,\Phi_n\rangle$ can be written

$$P\,|\,\Phi_n\rangle=(P_1+P_2)\,|\,\Phi_n\rangle \tag{16a}$$

$$=\left[\frac{\varphi_0(2,3)}{\sqrt{(4\pi)}}\Big\rangle\left[1+\sum_\alpha\frac{v_\alpha(r_1)\rangle\langle v_\alpha(r_1)}{\lambda_\alpha-1}\right]\Big\langle\frac{\varphi_0(2,3)}{\sqrt{(4\pi)}}+\frac{\varphi_0(3,1)}{\sqrt{(4\pi)}}\Big\rangle\left[1+\sum_\alpha\frac{v_\alpha(r_2)\rangle\langle v_\alpha(r_2)}{\lambda_\alpha-1}\right]\Big\langle\frac{\varphi_0(3,1)}{\sqrt{(4\pi)}}\right]|\,\Phi_n\rangle\,. \tag{16b}$$

Using Eq. (16b), expand $|\,\Phi_n\rangle$ as in Eq. (15a) and gather terms to obtain

$$P\,|\,\Phi_n\rangle=\left[\frac{\varphi_0(2,3)}{\sqrt{(4\pi)}}\Big\rangle\left[1+\sum_\alpha\frac{v_\alpha(r_1)\rangle\langle v_\alpha(r_1)}{\lambda_\alpha-1}\right]\int\frac{S(1)}{\sqrt{(4\pi)}}d\hat{\mathbf{r}}_1-\frac{\varphi_0(3,1)}{\sqrt{(4\pi)}}\Big\rangle\left[1+\sum_\alpha\frac{v_\alpha(r_2)\rangle\langle v_\alpha(r_2)}{\lambda_\alpha-1}\right]\int\frac{S(2)}{\sqrt{(4\pi)}}d\hat{\mathbf{r}}_2\right]\langle\varphi_0\,|\,UW\rangle-2\left(\begin{smallmatrix}SUW\\UWS\end{smallmatrix}\right)+\left(\begin{smallmatrix}SUW\\WSU\end{smallmatrix}\right)\,, \tag{17}$$

where the last two terms represent cyclic permutations of the explicitly given term (in the notation of Ref. 3), and

$$\langle\varphi_0\,|\,UW\rangle=\int\varphi_0(2,3)U(2)W(3)d^3r_2d^3r_3\,. \tag{18}$$

Since Q equals $1-P$ and the terms in parentheses in Eq. (17) are related by an interchange of coordinates 1 and 2, $Q\mid\Phi_n\rangle$ can be expressed in a simple form,

$$Q\mid\Phi_n\rangle=[I-(12)][I+(31)][\,|S(1)U(2)W(3)\rangle+\tfrac{1}{2}\,|\varphi_0(3,1)\mathcal{S}(2)\rangle\langle\varphi_0|UW\rangle-|\varphi_0(3,1)\mathcal{U}(2)\rangle\langle\varphi_0|WS\rangle$$
$$+\tfrac{1}{2}\,|\varphi_0(3,1)\mathcal{W}(2)\rangle\langle\varphi_0|SU\rangle]\,, \tag{19}$$

where we have defined the projected orbitals $\mathcal{S}(1)$ by

$$\mathcal{S}(1)\equiv\frac{1}{\sqrt{(4\pi)}}\int\frac{S(1)}{\sqrt{(4\pi)}}d\hat{\mathbf{r}}_1+\sum_\alpha\frac{v_\alpha(r_1)}{\sqrt{(4\pi)}}\int\frac{v_\alpha(r_1)S(1)}{(\lambda_\alpha-1)\sqrt{(4\pi)}}d^3r_1\,, \tag{20}$$

with similar definitions for $\mathcal{U}$ and $\mathcal{W}$.

C. Matrix elements of QHQ

An old configuration-interaction (CI) program[7] was modified so as to perform projection-operator calculations. In addition to the standard CI matrix elements, the new version of the program evaluates the projected overlap and Hamiltonian integrals (R, T, and V are another triple of spatial orbitals occurring in Φ),

$$G_1\equiv\langle R(1)T(2)V(3)[I+(13)][I-(21)]\,|\,\varphi_0(3,1)\mathcal{G}(2)\rangle\,, \tag{21a}$$

$$H_1\equiv\langle R(1)T(2)V(3)[I+(13)][I-(21)]\,|\,H\,|\,\varphi_0(3,1)\mathcal{G}(2)\rangle\,, \tag{21b}$$

$$H_2\equiv\langle\mathcal{T}(2)\varphi_0(3,1)[I-(21)]\,|\,H\,|\,\varphi_0(3,1)\mathcal{G}(2)\rangle\,, \tag{21c}$$

where $\mathcal{G}$ can be any one of $\mathcal{S}$, $\mathcal{U}$, or $\mathcal{W}$, and similarly $\mathcal{T}$ can be any one of similar integrals involving R, T, or V. The Hamiltonian is given by

$$H=h(1)+h(2)+h(3)+\frac{1}{r_{12}}+\frac{1}{r_{23}}+\frac{1}{r_{31}}\,, \tag{22}$$

with

$$h(i)\equiv-\tfrac{1}{2}\nabla_i^2-\frac{2}{r_i}\,. \tag{23}$$

Since the target and kernel eigenfunctions remain constant during the variational process, the integrals

$$\langle v_\alpha(2)\,|\,h(2)\,|\,v_\beta(2)\rangle\,, \tag{24a}$$

$$\left\langle\varphi_0(3,1)\left|h(1)+h(3)+\frac{1}{r_{13}}\right|\varphi_0(3,1)\right\rangle\,, \tag{24b}$$

$$\langle v_\alpha(2)\varphi_0(3,1)[I-(21)]\,|\,H\,|\,\varphi_0(3,1)v_\beta(2)\rangle\,, \tag{24c}$$

the HP terms in QHQ

$$h(2)v_\alpha(2)\,, \tag{25a}$$

TABLE I. Full and quasi-projection-operator energies ($\mathcal{E},\hat{\mathcal{E}}$) in eV for the lowest e^--He resonance, He$^-$[$1s(2s)^2{:}{}^2S$]. Calculations are based on a 40-term configuration-interaction wave function.[a] One hartree is taken as 27.211 608 eV.

Target	Target Energy $-\hat{E}_0$	Quasi-projection $\hat{\mathcal{E}}-E_0$	Full projection results $\mathcal{E}-E_0$	$\mathcal{E}-\hat{E}_0$
Closed shell	77.489	19.366[b]	19.593[c]	18.067[c]
Open shell	78.251	19.385[b]	19.666	18.908
$\mid 1s\,1s'\mid+\mid 2p\,2p\mid$	78.782[d]	19.388	19.615	19.382
4-term Hylleraas	78.9666	19.381	19.496	19.448
10-term Hylleraas	79.0091	19.379	19.504	19.499

Exact target energy,[e] $E_0=79.0150$ eV

Experimental resonance,[f] $\mathcal{E}-E_0=19.367\pm0.007$ eV

[a] The terms included in the CI wave function were $|(2s\,2s)1s|$, $|(1s\,2s)3s|$, $|(2s\,3s)1s|$, $|(1s\,2p)2p|$, $|(1s\,2p)3p|$, $|(1s\,3p)2p|$, $|(1s\,3p)3p|$, $|(1s\,3d)3d|$, $|(2s\,2p')2p'|$, $|(2s\,2p)2p'|$, $|(2s\,2p')2p|$, $|(2s\,2s')3s|$, $|(2s'3s)2s|$, $|(2s'2s')3s|$, $|(3s\,2p')2p'|$, $|(2p'2p)3d|$, $|(2p\,3d)2p'|$, $|(2p'2p')3d|$, $|(2p'3p)3d|$, $|(3p\,3d)2p'|$, $|(2s'2s')2s|$, $|(1s\,2s)4s|$, $|(2s\,4s)1s|$, $|(2s\,4s)1s|$, $|(3s\,3s)1s|$, $|(1s\,2p)4p|$, $|(1s\,4p)2p|$, $|(1s\,4d)3d|$, $|(1s\,4d)4d|$, $|(1s\,4f)4f|$, $|(1s\,2s)5s|$, $|(2s\,5s)1s|$, $|(1s\,2p)5p|$, $|(1s\,5p)2p|$, $|(1s\,3s)4s|$, $|(3s\,4s)1s|$, $|(1s\,3p)4p|$, $|(1s\,4p)3p|$, $|(3s\,2p)2p'|$, and $|(3s\,2p')2p|$.

[b] In Ref. 8, a hartree was assumed equal to 27.207 eV. Also, the quasi-resonance values reported here were obtained with different orbital exponents.

[c] This value was obtained from the open-shell limit; cf. Ref. 5.

[d] Reference 9.

[e] C. L. Pekeris, Phys. Rev. 112, 1649 (1958).

[f] Reference 11.

$$[H-h(2)]\varphi_0(3,1)\,, \tag{25b}$$

and the *PHP* terms in *QHQ*

$$\varphi_0(3,1)\frac{1}{r_{12}}\varphi_0(3,1)\,, \tag{26a}$$

$$\varphi_0(2,3)H\varphi_0(3,1)\,, \tag{26b}$$

can be evaluated prior to optimization of $|\Phi\rangle$. Details of the evaluation of three electron Hylleraas integrals as occurring, for example, in Eq. (24c) are presented in the Appendix.

III. RESULTS AND DISCUSSION

In these calculations the ^2S resonant state is represented as a 40-term CI wave function (cf. Table I). Orbitals are chosen to be of Slater type. For all targets studied, additional terms were included in the wave function and found to lower the *QHQ* eigenvalues by at most a few meV after the orbital exponents were reoptimized. (Each orbital has its own nonlinear parameter; thus the total Φ has 14 nonlinear parameters, in addition to its 40 linear parameters, and it represents a high quality variational ansatz for the accuracies involved here.)

Initially, two different ^1S He target approximations were used—a closed-shell ($E_0=-77.489$ eV)

$$\varphi_0(1,2)=N_\gamma e^{-\gamma(r_1+r_2)},\quad \gamma=1.6875 \tag{27}$$

and an open-shell target ($E_0=-78.251$ eV)

$$\varphi_0(1,2)=N_{\gamma_1\gamma_2}(e^{-\gamma_1 r_1-\gamma_2 r_2}+e^{-\gamma_1 r_2-\gamma_2 r_1})\,, \tag{28}$$

with

$$\gamma_1=2.1832,\quad \gamma_2=1.1886\,.$$

Results are given in Table I together with results from a previous quasiprojection-operator calculation.[8] The latter showed little dependence on target quality. In contrast, the present *QHQ* eigenvalue *increases* by 0.073 eV in going from the closed- to the open-shell target. This is caused by kernel eigenvalues (λ_α) near unity which make the contribution of kernel eigenfunctions to the eigenvalue problem significant. If a polarization term $[(2p)^2]$ is added to the open-shell function,[9] the target energy drops by more than half an eV. Again, the change in the quasi-projection estimate of the resonance position is small while the lowest *QHQ* eigenvalue now *decreases* by 0.041 eV.

Table I also contains results using a Hylleraas-type target function with four linear terms corresponding to $\omega=1$, discussed above, and also a 10-term Hylleraas-type target, corresponding to $\omega=2$. Values of the respective linear and nonlinear parameters are given in Table II.

TABLE II. Optimized parameter set for open-shell Hylleraas targets, Eq. (27).

	$\omega=1$	$\omega=2$
γ_1	2.05	2.05
γ_2	1.50	1.75
C_{000}	6.047 87	6.197 24
C_{100}	−4.407 77	−3.314 95
C_{010}	0.999 09	3.014 86
C_{001}	1.602 22	2.049 85
C_{200}		−0.872 00
C_{020}		1.642 49
C_{002}		−0.353 99
C_{110}		−0.199 20
C_{101}		1.556 11
C_{011}		−0.689 53

The *QHQ* eigenvalues relative to E_0 are seen to fluctuate; this suggests that the resonance position might be better measured relative to the appropriate approximate target energy, $\hat{E}_0$. When this comparison is made, the resonance position does indeed vary monotonically, but it is seen to overshoot the experimental result as the target state is improved, particularly for a many-parameter Hylleraas form.

Comparing the two types of resonance calculations, one might be tempted to conclude that the quasi-projection-operator technique is better than the complete projection-operator approach. We believe that such a conclusion would be unwarranted. Although quasi-projection-operators do have the essential property of yielding a discrete spectrum, $\hat{\mathscr{E}}_n$ (of $\hat{Q}H\hat{Q}$) in the midst of the continuum,[8,2] that technique does not yield a rigorous way of defining a shift, which is necessary for a determination of the exact position of a resonance, $E_{\text{res}}=\mathscr{E}+\Delta$, in the Feshbach theory. On the other hand, a well-defined expression for Δ does exist for true projection-operator calculations, and we believe that the real implication of our results is that the contribution of Δ is essential. Furthermore, we believe that such calculations may also allow for the construction of an optical potential, $\mathscr{V}_{\text{op}}$, from which truly convergent nonresonant phase shifts can also be calculated. (It will be recalled that our quasi-optical potential calculations did not converge[10] even though they were monotonically increasing with the number of terms in the ansatz for Φ.)

In the present case, this would imply that Δ [which can be expressed as a principle value involving $\Gamma(E')$] is quite different from the width $\Gamma=\Gamma(E_n)$ which is known to be approximately[11] 0.01 eV in this case. The calculation of the shift and width is now in progress.

APPENDIX

We shall consider the integral I of three-electron Hylleraas integrals with spherical harmonics,[12] Y_{LM}, included

$$I\equiv\int r_A^{N_A} r_B^{N_B} r_C^{N_C} r_{AB}^{N_{AB}} r_{BC}^{N_{BC}} r_{CA}^{N_{CA}} e^{-p_A r_A-p_B r_B-p_C r_C} Y_{L_R-M_R}(\hat{\mathbf{r}}_A)Y_{L_S M_S}(\hat{\mathbf{r}}_A)Y_{L_T-M_T}(\hat{\mathbf{r}}_B)Y_{L_U M_U}(\hat{\mathbf{r}}_B)Y_{L_V-M_V}(\hat{\mathbf{r}}_C)Y_{L_W M_W}(\hat{\mathbf{r}}_C)$$
$$\times d\hat{\mathbf{r}}_A d\hat{\mathbf{r}}_B d\hat{\mathbf{r}}_C dr_A dr_B dr_C\,. \tag{A1}$$

Basically, these integrals can be divided into two classes depending upon whether or not the integers N_{AB}, N_{BC}, and N_{CA} are all odd. If at least one of these integers is even, then I can be reduced to a finite sum of radial integrals. When all the interelectronic distances are raised to an odd power, the three-particle integrals will contain an infinite sum over angular momentum states.

Although methods for calculating integrals above have been given,[13] we have found them to be numerically unstable or inefficient. We therefore rederive them here in a form which is particularly well suited for numerical evaluation.

The interelectronic distance can be expanded using Sack's formula[14]

$$r_{AB}^{N_{AB}}=\sum_{L_{AB}} R_{N_{AB}L_{AB}}(r_A,r_B)P_{L_{AB}}(\hat{\mathbf{r}}_A\cdot\hat{\mathbf{r}}_B) \quad (N_{AB}\geq -1) \tag{A2}$$

where $P_L(x)$ are the Legendre polynomials and

$$R_{NL}(r_1,r_2)=\frac{(-N/2)_L}{(1/2)_L}\sum_J \frac{(L-N/2)_J(-(N+1)/2)_J}{J!(L+3/2)_J} r_>^{N-(L+2J)} r_<^{L+2J} , \tag{A3}$$

$r_>$ and $r_<$ are defined as the greater and lesser, respectively, of r_1 and r_2, and $(x)_J$ is Pochhammer's symbol.[15] Although lengthy, the angular integration is straightforward, from which one obtains

$$\begin{aligned} I=&(-1)^{M_R+M_U+M_V}\\ &\times \sum_{L_{AB},L_{BC},L_{CA}} \Bigg[\sum_{M_{AB},M_{BC},M_{CA}} (-1)^{M_{CA}}\\ &\qquad\times \sum_{L_A,M_A} d(L_A,L_R,L_{AB},-M_A,-M_R,-M_{AB})d(L_AL_SL_{CA}M_AM_QM_{CA})\\ &\qquad\quad\times \sum_{L_B,M_B} d(L_B,L_T,L_{BC},-M_B,-M_T,-M_{BC})d(L_BL_UL_{AB}M_BM_UM_{AB})\\ &\qquad\qquad\times \sum_{L_C,M_C} d(L_C,L_V,L_{CA},-M_C,-M_V,-M_{CA})d(L_CL_WL_{BC}M_BM_WM_{BC}) \Bigg]\\ &\times \int r_A^{N_A} r_B^{N_B} r_C^{N_C} R_{N_{AB}L_{AB}}(r_A,r_B)R_{N_{BC}L_{BC}}(r_B,r_C)R_{N_{CA}L_{CA}}(r_C,r_A)\\ &\quad\times e^{-p_Ar_A-p_Br_B-p_Cr_C}dr_Adr_Bdr_C . \end{aligned} \tag{A4}$$

The Gaunt coefficient appearing above is defined in terms of the Wigner 3-j symbol[12]

$$d(L_1L_2L_3M_1M_2M_3)\equiv(-1)^{(|M_3|-M_3)/2}(2L_1+1)^{1/2}(2L_2+1)^{1/2}\begin{pmatrix} L_1 & L_2 & L_3\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} L_1 & L_2 & L_3\\ M_1 & M_2 & M_3\end{pmatrix} . \tag{A5}$$

As stated above, if N_{AB}, N_{BC}, or N_{CA} is even, the angular momentum sums remain finite. A basic integral of the form

$$\sigma_{N_1N_2N_3}=\int_0^\infty r_1^{N_1}e^{-(A_1+A_2+A_3)r_1}\int_0^\infty (r_1+r_2)^{N_2}e^{-(A_2+A_3)r_2}\int_0^\infty (r_1+r_2+r_3)^{N_3}e^{-A_3r_3}dr_3dr_2dr_1 \tag{A6}$$

must be calculated. These integrals are known to be integrable whenever the integers N_1, N_1+N_2+1, and $N_1+N_2+N_3+2$ are all non-negative. In practice, however, the three-electron Hylleraas problem does not require evaluation of the most general σ integral. We consider two cases which together encompass all necessary forms.

Case I. $N_1,N_2,N_3\geq 0$*.* For these integrals, the analytic expression for σ is stable and easily determined,

$$\begin{aligned}\sigma_{N_1N_2N_3}=&\frac{(N_1+N_2+N_3)!}{(A_1+A_2+A_3)^{N_1+N_2+N_3+1}}\sum_{i=0}^{N_3}\frac{(-N_3)_i}{(-N_1-N_2-N_3)_i}\frac{(A_1+A_2+A_3)^i}{A_3^{i+1}}\\ &\times\sum_{h=0}^{N_2+N_3-i}\frac{(-N_2-N_3+i)_h}{(-N_1-N_2-N_3+i)_h}\frac{(A_1+A_2+A_3)^h}{(A_2+A_3)^{h+1}} .\end{aligned} \tag{A7}$$

Case II. N_1, N_2+N_3+1, $N_1+N_2+1\geq 0$*, and not case I. Whenever* N_2 *or* N_3 *are negative,* the analytical expression for the σ integrals tend to be numerically unstable. For case II, the following numerically stable approach was derived. Replace the r_3 variable in Eq. (A6) with $x=(r_1+r_2)/(r_1+r_2+r_3)$ and exchange order of integration to obtain

$$\sigma_{N_1N_2N_3}=\int_0^1 x^{-N_3-2}\int_0^\infty r_1^{N_1}e^{-(A_1+A_2+A_3/x)r_1}\int_0^\infty (r_1+r_2)^{N_2+N_3+1}e^{-(A_2+A_3/x)r_2}dr_2dr_1dx . \tag{A8}$$

After integration over r_2 and r_3, a one-dimensional integral that can be evaluated with Gaussian quadratures remains,

$$\sigma_{N_1N_2N_3}=\int_0^1 x^{N_1+N_2+1}\sum_{i=0}^{N_2+N_3+1}\frac{(-N_2-N_3-1)_i}{(-N_1-N_2-N_3-1)_i}\frac{(A_2x+A_3)^{-i-1}dx}{(A_1x+A_2x+A_3)^{N_1+N_2+N_3+2-i}}\ . \tag{A9}$$

The sums in Eqs. (A7) and (A9) are numerically stable because all the terms are of the same sign.

In the projection calculation of the Schulz resonance, the three-electron integrals for which N_{AB}, N_{BC}, and N_{CA} are all odd involve only s orbitals,

$$I_0=\frac{1}{(4\pi)^3}\int r_A^{N_A}r_B^{N_B}r_C^{N_C}r_{AB}^{N_{AB}}r_{BC}^{N_{BC}}r_{CA}^{N_{CA}}e^{-p_Ar_A-p_Br_B-p_Cr_C}dr_Adr_Bdr_Cdr_Adr_Bdr_C\ . \tag{A10}$$

Although the method derived here for evaluating the three-electron integrals is generally valid, we will restrict our discussion to I_0 integrals. For these integrals, the angular integration simplifies considerably and Eq. (A4) reduces to

$$I_0=\int r_A^{N_A}r_B^{N_B}r_C^{N_C}e^{-p_Ar_A-p_Br_B-p_Cr_C}\sum_{L=0}^{\infty}\frac{R_{N_{AB}L}(r_A,r_B)R_{N_{BC}L}(r_B,r_C)R_{N_{CA}L}(r_C,r_A)}{(2L+1)^2}dr_Adr_Bdr_C\ . \tag{A11}$$

In the standard method[14] of performing these integrals, the sum over L is truncated and each L integral is evaluated analytically. Unfortunately, the convergence can often be slow and the sum has to be evaluated each time an orbital's exponent is altered. We present an alternative method that alleviates both of these problems.

At first, consider the region $r_A<r_B<r_C$. If R_{NL} is expressed in a form which makes clear the L dependence

$$R_{NL}(r_1,r_2)=(2L+1)\sum_J\frac{(-N-1)_{2J}}{(2J+1)!}\frac{(J-N/2)}{(J+3/2)_L}r_>^{N-(L+2J)}r_<^{L+2J} \tag{A12}$$

then I_0 over this region equals

$$\begin{aligned}I_0(A<B<C)=\sum_{J_{AB},J_{BC},J_{CA}}&\frac{(-N_{AB}-1)_{2J_{AB}}}{(2J_{AB}+1)!}\frac{(-N_{BC}-1)_{2J_{BC}}}{(2J_{BC}+1)!}\frac{(-N_{CA}-1)_{2J_{CA}}}{(2J_{CA}+1)!}\\&\times\int_0^\infty\int_0^{r_C}\int_0^{r_B}W\left[\frac{r_A^2}{r_B^2}\right]e^{-p_Ar_A-p_Br_B-p_Cr_C}r_A^{N_A+2J_{AB}+2J_{CA}}r_B^{N_B+N_{AB}-2J_{AB}+2J_{BC}}\\&\times r_C^{N_C+N_{BC}-2J_{BC}+N_{CA}-2J_{CA}}dr_Adr_Bdr_C\ ,\end{aligned} \tag{A13}$$

where

$$\begin{aligned}W(x)&\equiv W(N_{AB},N_{BC},N_{CA};J_{AB},J_{BC},J_{CA};x)\\&\equiv\sum_L\frac{(J_{AB}-N_{AB}/2)_L}{(J_{AB}+3/2)_L}\frac{(J_{BC}-N_{BC}/2)_L}{(J_{BC}+3/2)_L}\frac{(J_{CA}-N_{CA}/2)_L}{(J_{CA}+3/2)_L}(2L+1)x^L\ .\end{aligned} \tag{A14}$$

Change integration variables to $r=r_C$, $x=r_A/r_C$, and $y=r_B/r_C$ and rearrange the order of integration, then I_0 has the form

$$\begin{aligned}I_0(A<B<C)=\sum_{J_{AB},J_{BC},J_{CA}}&\frac{(-N_{AB}-1)_{2J_{AB}}}{(2J_{AB}+1)!}\frac{(-N_{BC}-1)_{2J_{BC}}}{(2J_{BC}+1)!}\frac{(-N_{CA}-1)_{2J_{CA}}}{(2J_{CA}+1)!}\\&\times\int_0^1\int_x^1\int_0^\infty W(x)e^{-(p_Ax+p_By+p_C)r}x^{N_A+2J_{AB}+2J_{CA}}y^{N_B+N_{AB}-2J_{AB}+2J_{BC}}\\&\times r^{N_A+N_B+N_C+N_{AB}+N_{BC}+N_{CA}+2}dr\,dy\,dx\ .\end{aligned} \tag{A15}$$

Integration over r and summation over the six spatial regions then yields the final expression for I_0

$$\begin{aligned}I_0=&(N_A+N_B+N_C+N_{AB}+N_{BC}+N_{CA}+2)!\\&\times\sum_{J_{AB},J_{BC},J_{CA}}\frac{(-N_{AB}-1)_{2J_{AB}}}{(2J_{AB}+1)!}\frac{(-N_{BC}-1)_{2J_{BC}}}{(2J_{BC}+1)!}\frac{(-N_{CA}-1)_{2J_{CA}}}{(2J_{CA}+1)!}\\&\times\int_0^1dx\,W(x)\int_x^1\left[\frac{x^{N_A+2J_{AB}+2J_{CA}}y^{N_B+N_{AB}-2J_{AB}+2J_{BC}}}{(p_Ax+p_By+p_C)^{N_A+N_B+N_C+N_{AB}+N_{BC}+N_{CA}+2}}\right.\\&\left.+\binom{ABC}{CAB}+\binom{ABC}{BCA}+(A\leftrightarrow B)+(B\leftrightarrow C)+(C\leftrightarrow A)\right]dy\ .\end{aligned} \tag{A16}$$

The integrals over y can easily be evaluated analytically; to avoid additional complexity, the general antiderivative has not been explicitly written.

The expression for I_0, Eq. (A16), has an extremely important feature—the infinite sum over angular momentum is included in the orbital exponent independent W functions, Eq. (A14). This implies that if a fixed-point numerical integration routine such as Gaussian quadratures is employed to perform the integration over x, the infinite sum can be included in the fixed weight factors. Of course, these modified weight factors do have to be determined for each (J_{AB}, J_{BC}, J_{CA}) triple. However, the different W functions are usually not independent, and recursion relationships between them can be derived.

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