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Triply excited states of three-electron atomic systems

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A formalism is discussed whereby many-electron systems may be described by a great number of product functions of different configurations in a manageable way. Calculations are made to find triply excited energy levels of three-electron atomic systems, using products of hydrogenic functions with a Z equal to that of the nucleus. Results for the lowest $^2P^o$ and $^2S^e$ levels in the Li isoelectronic sequence, $Z = 1$ to 10, are presented. The results of calculations for the energies of $^2D^e$ triply excited states in He^- are also reported. The calculated energies are compared with available experimental and other theoretical values. Finally, the lowest $^2S^e$ and two lowest $^2P^o$ energy levels in the isoelectronic sequence are fitted by a $1/Z$ perturbation expansion. It is seen that this expansion can be used to estimate the energy levels of such states for higher nuclear charges.

I. INTRODUCTION

The existence of certain discrete and quasistationary excited atomic states having narrow widths was known experimentally in the early 1930's in the electron scattering from different atomic targets, and also in the photoabsorption spectra of the rare gases.[1] These quasistationary levels lie in the continuous spectrum of the atom above the first ionization threshold.[2] If their coupling with the adjacent continuum is not zero, they decay spontaneously by electron emission.[3] Such states are not true eigenstates of the total Hamiltonian for the atom as are the stationary states and the continuum states. In the literature they are referred to as unstable, metastable, quasistationary or autoionizing. In nuclear physics such states are also known as compound states. They are also called "resonant states," or simply resonances, because their excitation and subsequent decay in different collision processes results in the appearance of asymmetric peaks in the cross section near the energies of these levels. In the independent-particle approximation these states are classified as multiply excited, whereas the stationary states are almost always singly excited. The decay of the multiply excited states by electron emission takes place according to the selection rules of "radiationless transitions," derived from the conservation of energy, total angular momentum, and parity. If one or more of these conservation laws cannot be satisfied, then the multiply excited state will not autoionize into the adjacent continuum. There are many examples of such metastable, multiply excited states. The literature contains several review articles on the experimental and theoretical evidence for the existence of quasistationary states in various atomic and molecular systems.[4-6]

To explain what we mean by singly, doubly, and in general multiply excited states of an atom or ion, we have drawn schematic diagrams [Figs. 1(a), 1(b)] for the energy levels of a three-electron atomic system. When possible, each level is assigned a single atomic configuration, but when a mixture of several configurations is needed to describe that state accurately, the symbolic notation $(n_1, n_2\alpha)$ is used (see Refs. 15 and 22 for details). For instance, the lowest $^1S^e$ doubly excited state in helium is made up of $(2s^2)+(2p^2)$ and so is classified as $(2, 2a)$. The second lowest $^1S^e$ state is mostly $(2s^2)$-$(2p^2)$ and is classified as $(2,2b)$. The ground-state configuration for the neutral atom (Li), and also positive ions (Be^+, etc.), is shown as $(1s^2\,2s)\,^2S^e$ [Fig. 1(a)]. Above the ground state there lie an infinite number of singly excited, stationary states of the atomic system. These levels converge to the first single-ionization limit for the three-electron system which corresponds to the ground state of the two-electron system plus one electron at rest at infinity. Above that lie the singly excited states of the two-electron system (e.g., Li^+). Each of these states (including the ground state) has an adjacent single-electron continuum of energy levels which begins at the particular state and extends to infinity. The lowest doubly excited state of He^-, $(1s2s^2)\,^2S^e$, which lies 19.35 eV[4] above the He ground state $(1s^2)\,^1S$ is shown in Fig. 1(b). This state is an example of a discrete, quasistationary state embedded in the continuum [in this case, the continuum of levels associated with the ground state of He, $(1s^2\epsilon l)\,^2S^e$, $\epsilon > 0$].[3]

Higher up in the diagram we see the first double-ionization limit, denoted by $(1s\epsilon l\epsilon' l')$ which corresponds to the ground state of the doubly ionized

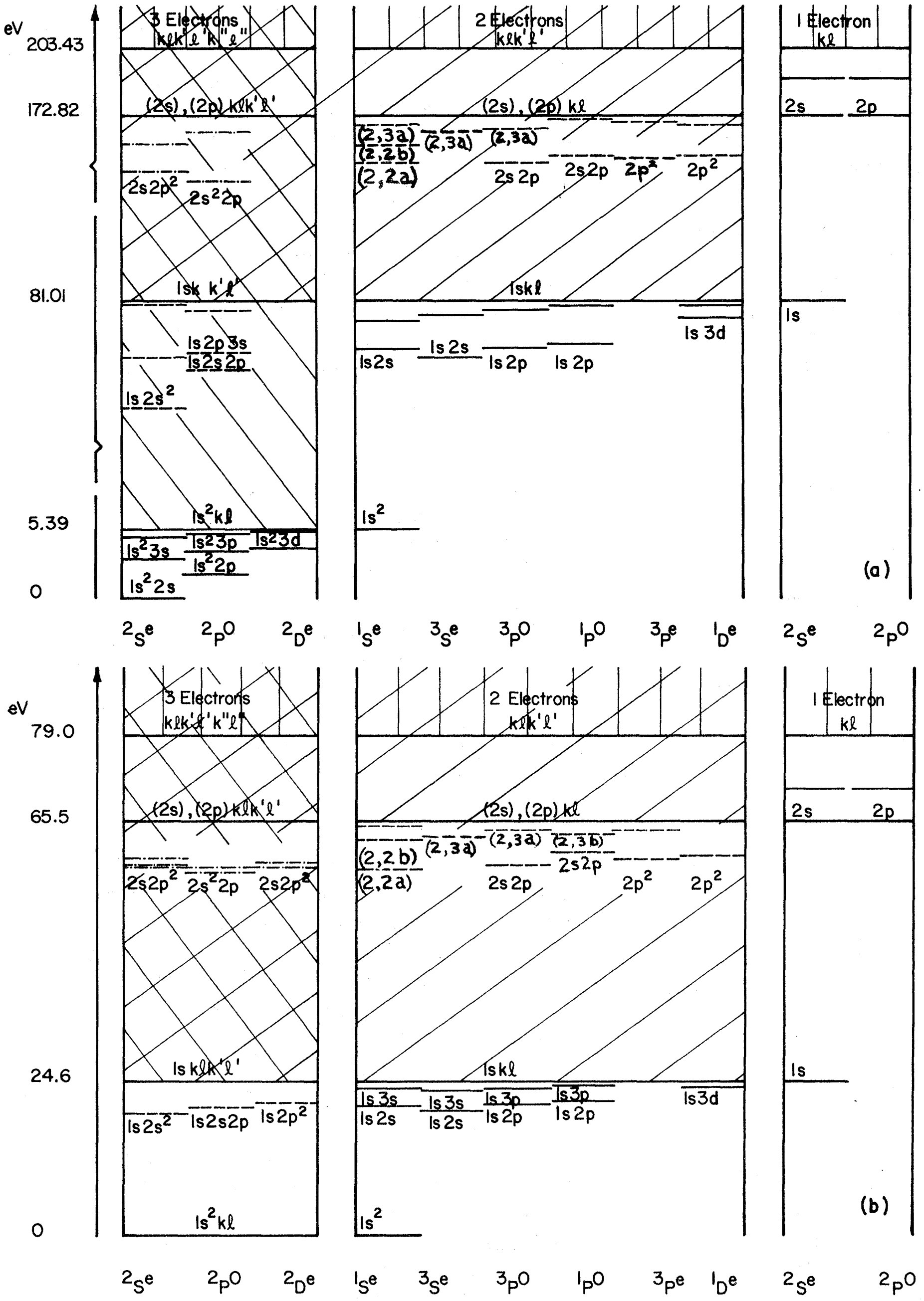

FIG. 1(a). Approximate energy level diagram for Li. Level designations are given according to independent particle model and Ref. 22. (b). Approximate energy level diagram for He$^-$. Level designations are given according to independent particle model and Ref. 22.

three-electron system with the other two electrons being at rest at infinity. For He the single-electron continuum starts at the ground state of He$^+$(1s), at 24.6 eV. The two degenerate excited levels of He$^+$, 2s and 2p, at 65.4 eV, form the second single-ionization limit of He. Below the 2s and 2p levels there exists an infinity of Rydberg series of doubly excited levels of He having symmetries $^{1,3}S^e$, $^{1,3}P^o$, $^{1,3}P^e$, $^{1,3}D^e$, $^{1,3}D^o$, etc. The three low-lying members, $(2,2a)\,^1S^e$ (at 57.9 eV), $(2s2p)\,^3P^o$ (at 58.4 eV), and $(2s2p)\,^1P^o$ (at 60.2 eV), are shown in the diagram. At around 59.7 eV there exists the $(2p^2)\,^3P^e$ doubly excited state of He. This is an example of a nonautoionizing state lying in the continuum, as it cannot spontaneously decay into He$^+$(1s) plus a free electron, without violating conservation of parity or angular momentum.

The existence of two triply excited states of He$^-$ with the configurations $(2s^2\,2p)\,^2P^o$ and $(2s2p^2)\,^2D^e$,[7] respectively, below the $(2,2a)\,^1S^e$ and $(2s2p)\,^3P^o$

doubly excited states of He [Fig. 1(b)] is experimentally well established.[8-11] Their energies are roughly 57.2 and 58.3 eV above the ground state of He. There have also been several theoretical calculations of these levels.[12-14] Grissom *et al.*[10] have reported two other resonance structures with energies around 58.79 and 59.4 eV, respectively, which have been interpreted as being due to the formation of ${}^2S^e$, triply excited states of He$^-$ by Smith *et al.*[14] These triply excited states are seen from the diagram to be embedded in the first double-electron continuum of the ground state of He$^+$, ($1s$), and also in the various single-electron continua associated with the singly and (in the case of ${}^2S^e$ and ${}^2D^e$ levels) doubly excited states of He. They can autoionize into the adjacent single- and double-electron continua by the following processes:

$$\begin{aligned}
(2s^2\,2p)\,{}^2P^o &\to (1snl)\,{}^{1,3}l+\epsilon(l\pm1) && \text{one-electron emission}\\
&\to 1s+\epsilon l+\epsilon'(l\pm1) && \text{two-electron emission}\\
(2s2p^2)\,{}^2D^e &\to 1s+\epsilon l+\epsilon'(l,l\pm2) && \text{two-electron emission}\\
&\to (1snl)\,{}^{1,3}l+\epsilon(l,l\pm2) && \text{one-electron emission}\\
&\to (2s^2)\,{}^1S+\epsilon d\to 1s+\epsilon' s+\epsilon d && \text{two-step one-electron emission}\\
(2s2p^2)\,{}^2S^e &\to 1s+\epsilon l+\epsilon' l && \text{two-electron emission}\\
&\to (1snl)\,{}^{1,3}l+\epsilon l && \text{one-electron emission}\\
&\left.\begin{aligned}&\to (2,2a)\,{}^1S+\epsilon s\to 1s+\epsilon s+\epsilon' s\\ &\to (2s2p)\,{}^3P+\epsilon s\to 1s+\epsilon p+\epsilon' p\end{aligned}\right\} && \\
& && \text{two-step one-electron emission.}
\end{aligned}$$

Generally speaking, an N-tuply excited state of a many-electron system is embedded in one to $(N-1)$-electron continua and can autoionize, giving up $1, 2, \ldots,$ up to $N-1$ free electrons.

With this introduction, we are now ready to present a method for the calculation of the energies of triply excited states in He$^-$ and other members of that isoelectronic sequence. The method is a modification and extension to three-electron atoms and ions of the procedure of truncated diagonalization (TDM).[6] The triply excited states of a three-electron system will be treated as being quasistationary bound states. This means that we suppose the system has been prepared to be in such a state at a certain instant by some excitation mechanism and persists in that state for a period of time equal to the mean lifetime of the state. To account for the well-defined existence of quasistationary states in various types of collision experiments, this time has to be much larger than both the excitation time and the period for the orbital motion of the electrons around the nucleus. The interaction is not known explicitly but it includes a part of the interelectron and the electron-nucleus potential terms of the total Hamiltonian for the system. In other words, the triply excited states are eigenstates of a part of the total Hamiltonian; the other part of the Hamiltonian induces the transition to the continuum states for those triply excited states which autoionize.

The quasistationary states can be treated theoretically as discrete, bound states which have well-defined energies and widths irrespective of the method employed for their excitation (preparation).[3,6] Further, we assume that a triply excited state of the three-electron system is formed as a result of the interaction between low-lying doubly excited two-electron targets and an additional electron. Therefore, its wave function can be represented by a linear combination of functions which are products of these doubly excited two-electron targets and one-electron functions. The various doubly excited targets are themselves described by coupled and totally antisymmetric configuration interaction (CI) wave functions, using hydrogenic basis functions with the nuclear charge Z. The additional one-electron functions are represented by the hydrogenic orbitals with the same nuclear charge Z. We will assume that L-S coupling is a good approximation for our purpose as we deal with light atoms (maximum value of $Z=10$) in the present work. Thus the triply excited wave functions are constructed to be the eigenfunctions of total L, S, and π, the parity for the state. To take into account the electron exchange, the wave function will be antisymmetrized with respect to the additional electron, as the doubly excited target functions are already antisymmetric in the two electrons. Such a wave function for the triply excited state is approximately orthogonal to all the lower-lying states with the same symmetry, including the discrete (singly and doubly excited) states and one- and two-electron continua. Since the low-lying three-electron states include in them the $1s$ orbital, and since the doubly excited states do not have a $1s$ orbital in them,[15] and the last electron orbitals are also orthogonal to $1s$, the wave function for the triply excited state is orthogonal to the low-lying states (exactly so in the independent-particle approximation). We will discuss this point later in more detail. The formalism for the calculations will be derived in Sec. II. In Sec. III we present the procedure and the results of calculations for the energies of several triply excited states in He$^-$, Li, Be$^+$, and other positive ions. In Sec. IV we give a general discussion of our method, and comment on certain related points.

II. MATHEMATICAL FORMALISM

A. General discussion

As discussed in Sec. I, we wish to represent the triply excited states of a three-electron system as a sum of products of doubly excited two-electron targets with one-electron functions. This requires the evaluation of the full three-electron Hamiltonian matrix with respect to the functions which are constructed by coupling a third electron to a two-electron wave function which is itself made up of many configurations. If we use two-electron functions which are coupled and properly symmetrized products of one-electron functions, then as will be shown here, the antisymmetrization with respect to the third electron can be carried out in either of two ways, giving rise to two choices of basis functions. One of these is the basis set of functions which are coupled and totally antisymmetric products of single configurations. The other, albeit much larger basis set, consists of coupled product functions of single configurations which are antisymmetric in electrons one and two but not in three. In the latter case, the three-electron antisymmetrization operator A will be incorporated explicitly in the various matrices arising in the formalism. When the number of different three-electron configurations is very large, using the former choice of basis functions requires a somewhat tedious and complicated procedure for evaluating the "coefficients of fractional parentage" (CFP), and removing the degeneracies associated with "seniority."[16] The second choice of bases recasts the formalism in an elegant and simple way such that questions regarding seniority do not arise, and an explicit formula can be used which avoids some of the problems of CFP's. Much of what follows is applicable to any N-electron system, but when explicitness is desired, we will focus on three-electron systems, since the formalism will specifically be applied to evaluate the energy levels for the triply excited states in He$^-$, Li, Be$^+$, and other positive ions of that isoelectronic sequence.

We are interested in working with three-electron functions of the form:

$$\begin{aligned}\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3) &= A\sum_{m_3\mu_3}(L_{12}l_3L|M_{12}m_3M)(S_{12}\tfrac{1}{2}S|\mu_{12}\mu_3M_s)\\ &\quad\times\psi(\vec{r}_1,\vec{r}_2)\varphi_{n_3l_3}(\vec{r}_3)\\ &\equiv A[\psi(\vec{r}_1,\vec{r}_2)\varphi_{n_3l_3}(\vec{r}_3)]_{LS}^{MM_s}, \qquad (1)\end{aligned}$$

where A is the three-electron antisymmetrization operator, and

$$\varphi_{nl}(\vec{r}) = R_{nl}(r)Y_l^m(\hat{r})\chi_{1/2}^{\mu} \qquad (2)$$

is a single-particle function. The dependence of ψ and φ on the magnetic quantum numbers M_{12}, m_3, μ_{12}, and μ_3 are shown explicitly in Eqs. (2) and (3) although they do not appear in Eq. (1). The brackets $[\ ]_{LS}^{MM_s}$ will be used at times to denote that the terms inside have been coupled together to give total $\vec{L}$ and $\vec{S}$. The $\psi(\vec{r}_1,\vec{r}_2)$'s are themselves expressible in terms of linear combinations of product functions. Thus we have

$$\psi_i(\vec{r}_1,\vec{r}_2) = \sum_j \alpha_{ij}\,\phi_j(\vec{r}_1,\vec{r}_2), \qquad (3a)$$

where

$$\phi(\vec{r}_1,\vec{r}_2) = \left[\frac{R_{n_1l_1}(1)R_{n_2l_2}(2)\mathcal{Y}_{L_{12}l_1l_2}^{M_{12}}(\hat{1},\hat{2}) + (-1)^{S_{12}}R_{n_1l_1}(2)R_{n_2l_2}(1)\mathcal{Y}_{L_{12}l_1l_2}^{M_{12}}(\hat{2},\hat{1})}{(\sqrt{2}+(2-\sqrt{2})\delta_{n_1n_2}\delta_{l_1l_2})}\right]\chi_{S_{12}}^{\mu_{12}}(1,2) \qquad (3b)$$

and

$$\mathcal{Y}_{Ll_1l_2}^{M}(\hat{1},\hat{2}) = \sum_{m_1,m_2}(l_1l_2L|m_1m_2M)Y_{l_1}^{m_1}(\hat{1})Y_{l_2}^{m_2}(\hat{2}). \qquad (3c)$$

The R_{nl}'s are mutually orthonormal but otherwise unspecified, although in our application, we will use hydrogenic functions with a Z equal to that of the nucleus. The Y_l^m's are the usual spherical harmonics, the χ's are spin functions, and $(l_1l_2L|m_1m_2M)$ is a Clebsch-Gordan coefficient as defined in Rose.[17] The α's are CI coefficients which presumably come from having previously diagonalized some two-electron Hamiltonian matrix, thereby making $\psi_i(\vec{r}_1,\vec{r}_2)$ a reasonable approximation to some two-electron wave function with energy E_i. In our application, the ψ_i's will be CI wave functions for various doubly excited states of the two-electron atomic core of He, Li$^+$, etc. as calculated by the TDM[6,15] without 1*s* orbitals. We note that $\alpha_{ij}=0$ unless $L_i=L_j$, $S_i=S_j$, $M_i=M_j$, and $\mu_i=\mu_j$.

The subscripts are somewhat ambiguous. We understand that the subscript i when associated with $\phi_i(\vec{r}_1,\vec{r}_2)$ stands for a set of values

$$i\equiv\{n_1l_1,n_2l_2,L_{12},M_{12},S_{12},\mu_{12}\}.$$

The subscript i when used with $\psi_i(\vec{r}_1,\vec{r}_2)$ will stand for the set

$$i\equiv\{L_{12},M_{12},S_{12},\mu_{12},E_i\}.$$

On the other hand, when i is used as a subscript for Ψ_i, it stands for the set of quantum numbers

$$i\equiv\{L_{12},S_{12},n_3,l_3,E_i,L,S\}.$$

The functions defined in Eq. (1) are linearly independent, but not orthogonal (except in trivial cases). An orthonormal basis set can be constructed by first evaluating the overlap matrix:

$$X_{ij}=\langle\Psi_i|\Psi_j\rangle. \tag{4}$$

X is Hermitian and has no negative eigenvalues. The vectors defined by

$$|\bar{\Psi}_i\rangle=\sum_j(\Lambda^{-1/2}U)_{ij}|\Psi_j\rangle, \tag{5}$$

where Λ and the unitary matrix U satisfy the eigenvalue equation

$$UXU^{-1}=\Lambda=\Lambda^{1/2}\Lambda^{1/2},$$

form the desired orthonormal basis set which spans the same space as the Ψ_j's. The orthonormality is easily shown:

$$\begin{aligned}\langle\bar{\Psi}_k|\bar{\Psi}_i\rangle&=\sum_{j,l}(\Lambda^{-1/2}U)_{ij}(\Lambda^{-1/2}U)_{kl}\langle\Psi_l|\Psi_j\rangle\\&=(\Lambda^{-1/2}UX\tilde{U}\Lambda^{-1/2})_{ki}=(\Lambda^{-1/2}\Lambda\Lambda^{-1/2})_{ki}\\&=(I)_{ki}=\delta_{ki}.\end{aligned}$$

The next step is to construct the Hamiltonian matrix with respect to this orthonormal basis:

$$\mathcal{H}_{ij}=\langle\bar{\Psi}_i|H|\bar{\Psi}_j\rangle, \tag{6a}$$

where

$$\begin{aligned}H&=\left[-\sum_{i=1}^{3}\left(\tfrac{1}{2}\nabla_i^2+\frac{Z}{r_i}\right)+\left(\frac{1}{r_{12}}+\frac{1}{r_{23}}+\frac{1}{r_{13}}\right)\right]\\&=H_1+H_2+H_3+V_{12}+V_{23}+V_{13}\end{aligned} \tag{6b}$$

is the standard three-electron Hamiltonian (expressed in atomic units) in the field of nuclear charge Z. The eigenvalues of $\mathcal{H}$ can be thought of as representing the energy levels associated with the operator QHQ, where Q is the projection operator onto the subspace spanned by the Ψ_i's and can be written as

$$Q\equiv\sum_{i=1}^{n}|\bar{\Psi}_i\rangle\langle\bar{\Psi}_i|, \tag{7a}$$

where n is the dimension of the subspace spanned by the $|\bar{\Psi}_i\rangle$'s. We have

$$Q|\bar{\Psi}_j\rangle=|\bar{\Psi}_j\rangle, \tag{7b}$$

and for an arbitrary function $|f\rangle$,

$$Q|f\rangle=0 \tag{7c}$$

if and only if

$$\langle\bar{\Psi}_i|f\rangle=0\quad\text{for all } i=1,n. \tag{7d}$$

It easily follows that

$$\langle\bar{\Psi}_i|QHQ|\bar{\Psi}_j\rangle=\langle\bar{\Psi}_i|H|\bar{\Psi}_j\rangle=\mathcal{H}_{ij}. \tag{7e}$$

B. Method

First of all, we will use the basis set of three-electron product functions which are antisymmetric in particles one and two, but not in three. All the above functions will be expressed in terms of these:

$$\begin{aligned}&\Phi_i(1,2;3|n_1l_1,n_2l_2,L_{12},S_{12},n_3l_3,L,S)\\&\qquad\equiv[\phi_i(1,2)\varphi_{n_3l_3}(3)]_{LS}^{MM_S}.\end{aligned} \tag{8}$$

We define now the three-electron antisymmetrization operator as

$$A=\frac{1}{3!}\left(\sum_{p=1}^{3!}(-1)^p\mathcal{P}_p\right),$$

where the sum is over all permutations of three particles. With this definition, A has the property that $A^2=A$, and $A=A^\dagger$. That is, A is idempotent and Hermitian; therefore A is a projection operator.[18]

We have to calculate the matrix representation of A in terms of the functions of Eq. (8). Thus we have

$$A\Phi_i=\sum_j A_{ij}\Phi_j.$$

$A_{ij}=0$ unless the single-particle quantum numbers $(n_1l_1,n_2l_2,n_3l_3)_j$ of function j are a permutation of those of function i. The Φ's are orthonormal, but the $A\Phi$'s are neither orthogonal nor normalized.

As an example, consider the three functions

$$\Phi_1(2s2s\,{}^1S\,2p\,{}^2P^o),$$

$$\Phi_2(2s2p\,{}^1P\,2s\,{}^2P^o),$$

$$\Phi_3(2s2p\,{}^3P\,2s\,{}^2P^o).$$

These three functions form an invariant subspace for A, in that A operating on any one of them will give a linear combination of them only. In this case, A has the three-dimensional representation:

$$[A]=\tfrac{1}{3}\begin{bmatrix} 1 & -1/\sqrt{2} & -\sqrt{3}/\sqrt{2} \\ -1/\sqrt{2} & 1/2 & \sqrt{3}/2 \\ -\sqrt{3}/\sqrt{2} & \sqrt{3}/2 & 3/2 \end{bmatrix}. \tag{9}$$

It is easy to see that $A\Phi_1, A\Phi_2, A\Phi_3$ are all proportional to each other, as required, since there is only one totally antisymmetric function in this three-dimensional space, and therefore the A matrix in Eq. (9) has only one nonzero eigenvalue. In Appendix A, we derive the explicit formula for A, for all cases.

We now express Ψ_i [Eq. (1)] in terms of α, A, and the Φ's:

$$\begin{aligned}\Psi_i &= A[\psi_i\varphi_{nl}]_{LS}^{MM_S} = A\Big[\sum_j \alpha_{ij}\phi_j\varphi_{nl}\Big]_{LS} \\ &= A\sum_j \alpha_{ij}[\phi_j\varphi_{nl}]_{LS} = A\sum_j \alpha_{ij}\Phi_j(1,2;3) \\ &= \sum_j \alpha_{ij}A\Phi_j = \sum_{j,k}\alpha_{ij}A_{jk}\Phi_k .\end{aligned} \tag{10}$$

The matrix α is rectangular and of order $n\times m$, where m denotes the dimension of the full configuration space spanned by the partly antisymmetric Φ's, and n is the dimension of the subspace spanned by the Ψ's. The matrix A is square and of order $m\times m$.

Next we evaluate X in the Φ basis. From Eq. (4) we have

$$\begin{aligned}X_{ij} &= \sum_{k,l,m,n} \alpha^*_{il}A^*_{lk}\alpha_{jm}A_{mn}\langle\Phi_k|\Phi_n\rangle \\ &= \sum \alpha^*_{il}A^*_{lk}A_{mn}\alpha_{jm}\delta_{kn} .\end{aligned}$$

But A is real and symmetric, so we have

$$\begin{aligned}X_{ij} &= \sum \alpha^*_{il}A_{lk}A_{mk}\alpha_{jm} = \sum \alpha^*_{il}A_{lk}A_{km}\alpha_{jm} \\ &= (\alpha AA\alpha^\dagger)_{ji} = (\alpha A\alpha^\dagger)_{ji} = (\alpha A\alpha^\dagger)_{ij} ,\end{aligned} \tag{11}$$

where $\alpha^*_{ij}=(\alpha^\dagger)_{ji}$, and we have made use of the fact that $A^2=A$. From Eqs. (5) and (10), we can now write down the relationship between the $\bar{\Psi}$'s and the Φ's.

$$\bar{\Psi}_i(1,2,3) = \sum_{j=1}^{m}(\Lambda^{-1/2}U\alpha A)_{ij}\Phi_j(1,2;3). \tag{12}$$

At this point, we stop to mention that the matrix

$$M \equiv (\Lambda^{-1/2}U\alpha A) \tag{13a}$$

has the properties

$$\begin{aligned}MM^\dagger &= \Lambda^{-1/2}U\alpha AA\alpha^\dagger U^{-1}\Lambda^{-1/2} \\ &= \Lambda^{-1/2}U\alpha A\alpha^\dagger U^{-1}\Lambda^{-1/2} \\ &= \Lambda^{-1/2}UXU^{-1}\Lambda^{-1/2} \\ &= \Lambda^{-1/2}\Lambda\Lambda^{-1/2} \\ &= I ,\end{aligned} \tag{13b}$$

but

$$M^\dagger M = A\alpha^\dagger X^{-1}\alpha A \neq I .$$

In fact,

$$Q = M^\dagger M \tag{14}$$

is the matrix representation in the Φ basis of the projection operator defined in Eqs. (7). Q has zero eigenvalues corresponding to the eigenvectors not lying in the subspace spanned by the Ψ's, while the eigenvectors of Q belonging to eigenvalue 1 all lie in this subspace.

We can now evaluate the Hamiltonian matrix [Eq. (6)]:

$$\begin{aligned}\mathcal{H}_{ij} &= \langle\bar{\Psi}_i|H|\bar{\Psi}_j\rangle \\ &= \sum_{k,l} M^*_{ik}H_{kl}M_{jl} = (MHM^\dagger)_{ij} ,\end{aligned} \tag{15a}$$

where

$$H_{kl} = \langle\Phi_k|H|\Phi_l\rangle . \tag{15b}$$

Note that Eq. (15b) is real and symmetric.

It is of interest to look further at the matrix QHQ. This is the type of matrix one uses in Feshback formalism to calculate autoionization resonances.[19] It can be shown that QHQ (with dimension space m of Φ space), has the same nonzero eigenvalues as $\mathcal{H}$ (with dimension n of Ψ space), since they are related by the following equations:

$$QHQ = M^\dagger MHM^\dagger M = M\mathcal{H}M^\dagger$$

and

$$\mathcal{H} = MQHQM^\dagger = MHM^\dagger .$$

Thus, by selecting a set of functions (i.e., the Ψ_i's) one has equivalently chosen a projection operator Q.

We now show that

$$\begin{aligned}\mathcal{H}_{ij} &= \sum_{l,k} M^*_{il}\langle\Phi_l(1,2;3)|3(H_3+V_{12})|\Phi_k(1,2;3)\rangle M_{jk} \\ &= 3(M\mathfrak{h}M^\dagger)_{ij} ,\end{aligned} \tag{16a}$$

where

$$\mathfrak{h} = H_3 + V_{12}, \tag{16b}$$

and H_3 and V_{12} are as defined in Eq. (6). First of all, consider

$$C_{lk} = \langle\Phi_l(1,2;3)|H_2+V_{13}|\Phi_k(1,2;3)\rangle . \tag{16c}$$

Since this represents an integral over all three particles, the labels 1 and 2 can be interchanged, leaving

$$C_{lk}=\langle\Phi_l(1,2;3)|H_1+V_{23}|\Phi_k(1,2;3)\rangle\rangle,$$

because

$$\Phi_l(1,2;3)=-\Phi_l(2,1;3)\equiv-P_{12}\Phi_l(1,2;3). \tag{17}$$

When the coordinates of particles 2 and 3 are relabeled, C_{lk} becomes

$$\begin{aligned}C_{lk}&=\langle\Phi_l(1,3;2)|H_3+V_{12}|\Phi_k(1,3;2)\rangle\rangle\\&=\langle P_{23}\Phi_l(1,2;3)|H_3+V_{12}|P_{23}\Phi_k(1,2;3)\rangle\rangle\\&=(P_{23}\mathfrak{h}P_{23})_{lk}.\end{aligned}$$

Recalling Eq. (13a), we have

$$\begin{aligned}\overline{C}_{ij}&\equiv(MCM^\dagger)_{ij}\\&=\sum_{l,k}M_{il}C_{lk}M^*_{jk}\\&=\sum_{l,m,n,k}(\Lambda^{-1/2}U\alpha)_{in}A_{nl}\langle P_{23}\Phi_l(1,2;3)|H_3+V_{12}|P_{23}\Phi_k(1,2;3)\rangle\rangle(\Lambda^{-1/2}U\alpha)^*_{jm}A^*_{mk}\\&=\sum_{m,n}(\Lambda^{-1/2}U\alpha)_{in}\left\langle P_{23}\left(\sum_l A_{nl}\Phi_l\right)\middle|\mathfrak{h}\middle|P_{23}\left(\sum_k A_{mk}\Phi_k\right)\right\rangle(\Lambda^{-1/2}U\alpha)^*_{jm}.\end{aligned}$$

It is not hard to show that

$$P_{23}A=AP_{23}=-A,$$

and since

$$\sum_l A_{nl}\Phi_l=A\Phi_n,$$

we get

$$\begin{aligned}\overline{C}_{ij}&=\sum_{m,n}(\Lambda^{-1/2}U\alpha)_{in}\langle-A\Phi_n|\mathfrak{h}|-A\Phi_m\rangle(\Lambda^{-1/2}U\alpha)^*_{jm}\\&=\sum_{k,l,m,n}(\Lambda^{-1/2}U\alpha)_{in}A_{nl}\langle\Phi_l|\mathfrak{h}|\Phi_k\rangle A^*_{mk}(\Lambda^{-1/2}U\alpha)^*_{jm}.\end{aligned} \tag{18a}$$

In effect, A has absorbed P_{23}, leaving

$$\overline{C}_{ij}=(M\mathfrak{h}M^\dagger)_{ij}, \tag{18b}$$

and so we have

$$\mathcal{H}=3M\mathfrak{h}M^\dagger.$$

Note that $\mathfrak{h}$ is block diagonal in form, in that $\mathfrak{h}_{ij}=0$ unless $L_i=L_j, S_i=S_j, l_{3i}=l_{3j}$.

One would similarly show that $\mathcal{H}$ can be written in the form:

$$\mathcal{H}=3M[\tfrac{1}{2}(H_1+H_2)+V_{12}]M=3M\overline{\mathfrak{h}}M^\dagger. \tag{19}$$

$\overline{\mathfrak{h}}_{ij}$ has the additional property that $\overline{\mathfrak{h}}_{ij}=0$, unless $n_{3i}=n_{3j}$, making it completely independent of the third electron function.

C. Relation of the a matrices with CFP and seniority

The treatment of product wave functions representing several equivalent electrons is exhaustively covered in the literature.[20] We would like to connect this with the formalism developed in Sec. II B. In the process we hope to gain some insight about totally antisymmetric basis functions in N electrons, and also about coefficients of fractional parentage and seniority schemes. Briefly, one would like to express a totally antisymmetric N-electron wave function in terms of sums of $(N-1)$-electron wave functions, which are multiplied by a one-electron function and then coupled together, i.e.,

$$\overline{\Phi}_i(1,2,\ldots,N|LS)=\sum_j a_{ij}[\phi_j(1,2,\ldots,N-1|L_jS_j)\varphi_j(r_N)]_{LS}=\sum_j a_{ij}\Phi_j(1,2,\ldots,N-1;N), \tag{20}$$

where

$$\Phi_i(1,2,\ldots,N-1;N)\equiv[\phi_i(1,2,\ldots,N-1|L_iS_i)\varphi_i(r_N|l_i)]_{LS}.$$

The sum is only over all those j's which have the same set of orbitals as i. The a_{ij}'s are generalizations of the coefficients of fractional parentage (CFP's). This decomposition is not necessarily unique. There may be two or more mutually orthonormal $\overline{\Phi}(1,\ldots,N)$'s with the same L and S, associated with a given set of orbitals (i.e., same set of $\{n_j l_j|j=1,N\}$). For example, for d^3 configurations, there are two functions with $L = 2$ and $S = \frac{1}{2}$. Racah[17] introduced the concept of seniority, so as to remove this degeneracy, and thereby allow the $\bar{\Phi}$'s to be uniquely specified. Any given orthonormal set of $\bar{\Phi}$'s is related to Racah's by a unitary transformation.

Consider now, the functions, $\Phi(1, \ldots, N-1; N)$. $A\Phi_i$ must be expressible as a linear combination of the $\bar{\Phi}$'s of Eq. (20), since the $\bar{\Phi}$'s span the space of completely antisymmetric functions. We can write

$$A\Phi_j(1,2,\ldots,N-1;N) = \sum_i b_{ji}\bar{\Phi}_i(1,2,\ldots,N) \tag{21a}$$

and

$$\begin{aligned} A_{ij} &= \langle\Phi_i|A|\Phi_j\rangle = \sum_k b_{jk}\langle\Phi_i|\bar{\Phi}_k\rangle \\ &= \sum_k b_{jk}a_{ki} = (ba)_{ji}\,. \end{aligned} \tag{21b}$$

Since $A_{ij} = A_{ji}$, we have

$$A_{ij} = (ba)_{ij}\,. \tag{22}$$

Recall that the Φ's and also the $\bar{\Phi}$'s are orthonormal sets, so from Eqs. (20) and (21a)

$$\begin{aligned} a_{ji} &= \langle\Phi_i|\bar{\Phi}_j\rangle = \langle\Phi_i|A\bar{\Phi}_j\rangle \\ &= \langle A\Phi_i|\bar{\Phi}_j\rangle = b_{ij}\,, \end{aligned}$$

or

$$b^T = a, \tag{23}$$

and from Eqs. (22) and (23)

$$A = a^T a. \tag{24}$$

Because of the orthonormality of $\bar{\Phi}_i$'s and Φ_i's, we have

$$\begin{aligned} \delta_{ij} &= \langle\bar{\Phi}_i|\bar{\Phi}_j\rangle \\ &= \sum_{k,l} a_{ik}a_{jl}\langle\Phi_k|\Phi_l\rangle \\ &= \sum_k a_{ik}a_{jk} \end{aligned}$$

or

$$aa^T = I.$$

The a_{ij}'s are generalized CFP's but they are not uniquely defined because of the fact that the $\bar{\Phi}$'s are not unique to within an arbitrary orthogonal transformation (unless there is only one $\bar{\Phi}$). But, A is not dependent on what seniority scheme is picked, since different schemes are related by unitary transformations. Let a and a' be two different sets of CFP's derived from different schemes; then

$$a' = Ua, \tag{25}$$

where

$$U^{-1} = U^T;$$

so

$$\begin{aligned} A' &= a'^T a' = (Ua)^T Ua = a^T U^T Ua \\ &= a^T U^{-1} Ua = a^T I a = a^T a = A. \end{aligned}$$

We can look at A from an alternate point of view. Suppose the $\bar{\Phi}_i$'s span an n-dimensional subspace of the m-dimensional space, spanned by the Φ_i's. Let A_{ij} be an m-dimensional representation of A. Since

$$A^2 = A,$$

all the eigenvalues of A must be either 0 or 1. Also, as A is real-symmetric, there exists an orthogonal matrix U, such that

$$UAU^{-1} = \begin{bmatrix} I_{(n)} & 0 \\ 0 & 0_{(m-n)} \end{bmatrix}, \tag{26}$$

where n equals the multiplicity of eigenvalue $\lambda = 1$, and $(m-n)$ is the multiplicity of the zero eigenvalue. The n-dimensional subspace is spanned by the totally antisymmetric functions. Now

$$\begin{bmatrix} I_{(n)} & 0 \\ 0 & 0_{(m-n)} \end{bmatrix} = a_0^T a_0, \tag{27a}$$

where

$$\begin{bmatrix} 1 & 0 & 0 & 0 & \cdot & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & \cdot & 0 & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 1 & \cdot & 0 & 0 & 0 & 0 \end{bmatrix} = [I_n \;\; 0] \tag{27b}$$

is an n-row by m-column array. Consequently,

$$A = U^{-1}a_0^T a_0 U = U^T a_0^T a_0 U = (a_0 U)^T(a_0 U) = a^T a, \tag{28a}$$

where

$$a = a_0 U \tag{28b}$$

and

$$aa^T = I_{(n)} = a_0 a_0^T\,. \tag{28c}$$

The matrix a is seen to be rectangular (with the same dimensions as a_0) whose rows are orthonormal vectors. Any orthogonal rearrangement of these rows will also give a valid a, yielding the same A. Therefore, a can be written in the general form

$$a = U_1(n \times n)a_0(n \times m)U_2(m \times m). \tag{29}$$

U_1 corresponds to the arbitrary choice of the $\bar{\Phi}$'s and U_2 corresponds to the selection of the basis functions $\{\Phi_i\}$. There are two trivial cases, corresponding to $n=0$ (then $a_0=0$, $a=0$, and $A=0$) and $n=m$ (i.e., $a_0=I$, $a=U_1U_2$, and $a^Ta=A=I$). Otherwise, we have $1\leq n\leq m$. If $n=1$, then $U_1=1$, and a is uniquely defined by the choice of basis functions $\{\Phi_i\}$.

In Appendix A, we shall derive a relationship between A and the exchange operator P_{ij} using the $\{\Phi_i\}$ as the basis functions, and then evaluate the matrix A explicitly for three particles. Once we have done this, we may calculate some a, if necessary, by observing that since

$$A=a^Ta=U_2^Ta_0^Ta_0U_2,\quad a=a_0U_2$$

we have

$$U_2AU_2^T=a_0^Ta_0. \tag{30}$$

But $a_0^Ta_0$ is diagonal, so U_2 is an orthogonal matrix which diagonalizes A. Since, in general, the eigenvalues of A are not all distinct, there exist many such orthogonal matrices which satisfy Eq. (30).

In the above discussion we have only used the properties of A which make it a projection operator; thus everything shown is true for all projection operators. The a matrices for two different cases are evaluated in Appendix B.

D. Explicit use of totally antisymmetric bases

Since our objective is to evaluate the matrix $\mathcal{H}$ [Eqs. (16) and (17) in Sec. II B], we see that if we use CI target functions (nontrivial α), a knowledge of a is unnecessary. What we need instead are the eigenvalues and eigenvectors of $X=\alpha A\alpha^T$ [Eq. (11)]. If we include enough two-electron target states, so that α has the same dimension n, as a, then X will have the same dimension as the number of linearly independent, totally antisymmetric functions. Any further addition of target states will not increase the dimension of $\bar{\Phi}$ space, and X will have some zero eigenvalues. In any case, when α and a have the same dimensions, the eigenvalues of $\mathcal{H}$ will be identical with the Hamiltonian matrix derived from using totally antisymmetric functions directly, without concern for target states. The dimensions of the $\mathcal{H}$ matrix, in this case, however, can exceed 300, even if only one-electron orbitals through $n_1, n_2, n_3=5$ are included, so this procedure is not of practical use. In Sec. V C we discuss our results for ${}^2P^o$, where we calculate energies using five target states and all orbitals through $2\leq n_i\leq 4$, $l_i\leq 2$ and compare with calculations using all possible antisymmetric functions having the same orbitals. The former requires the diagonalization of a 21×21 Hamiltonian matrix, while the latter requires one which is well over 100×100.

III. CALCULATION OF THE ENERGIES OF TRIPLY EXCITED STATES

As discussed in Secs. I and II, we expanded the wave function of the triply excited states in a linear combination of products of low-lying doubly excited two-electron target functions, with various one-electron functions for the third electron. For example, in order to calculate the $(2s^2\,2p)\,{}^2P^o$ state in He⁻ we first diagonalized the particular truncated two-electron Hamiltonian, as in Refs. 6 and 15 to obtain the CI eigenfunctions (α matrix of Sec. II) for the lowest members of the five doubly excited He targets with symmetries ${}^1S^e$, ${}^1P^o$, ${}^3P^o$, ${}^3P^e$, and ${}^1D^e$. The two-electron functions were constructed using all possible hydrogenic orbitals with orbital angular momentum 0, 1, and 2, and principal quantum number $n=2, 3, 4, 5$. The charge Z used was the same as that of the nucleus. Hydrogenic single-particle orbitals were also used for the third electron function, using the formalism of Sec. II to construct the basis functions $\{\Phi_i\}$. The Hamiltonian matrix $\mathcal{H}$ [Eq. (17)] was then set up and diagonalized, yielding eigenvalues which are approximations to the various ${}^2P^o$ energy levels. All the energies calculated in this way are expressed in a.u. below the total ionization limit for the three-electron system (the zero of the energy). For He⁻ and Li some of the energies calculated here are also given in eV above the ground states of He and Li⁺, respectively. The conversion between eV and a.u. used is as follows:

$$\Delta E(\text{eV})=27.210\Delta E(\text{a.u.}), \tag{31a}$$

$$E_{\text{He}}(\text{eV})=78.9878-27.210|E_{\text{He}}(\text{a.u.})|, \tag{31b}$$

$$E_{\text{Li}^+}(\text{eV})=203.4303-27.210|E_{\text{Li}^+}(\text{a.u.})|, \tag{31c}$$

where $E_A(\text{eV})$ is the energy above the ground state of A.

The results of our calculation of the energy of the lowest ${}^2P^o$ state of He⁻ is given in Table I, together with several recent theoretical calculations and experimental measurements. Golden, Schowengerdt, and Macek[21] have pointed out that earlier experiments which used the $(1s2s^2)\,{}^2S$ resonance in He⁻ to calibrate their energy scales gave values for the triply excited states which were on the order of 0.05 eV too low, since they would have used the value of 19.3 eV instead of the presently accepted position of 19.35 eV.

Our value of 57.350 eV is in good agreement with the calculations of Nicolaides,[12] and Eliezer and Pan,[13] but the experiments of Kuyatt *et al.*,[8] Sanche and Schulz,[9] and Grissom *et al.*[10] all found a resonance about 0.2 eV below our value. This dis-

TABLE I. Position of $(2s^2 2p)^2P^o$ resonance in He$^-$.

Experiment (eV)	Theory (eV)	Present calculation (eV)
57.15 ± 0.04 [a]	57.3 [e]	57.350
57.1 ± 0.1 [b]	57.3 [f]	
57.16 ± 0.05 [c]	56.5 [g]	
57.21 [d]		

[a] Reference 11.
[b] Reference 8.
[c] Reference 9.
[d] Reference 10.
[e] Reference 13.
[f] Reference 12.
[g] Reference 14.

crepancy is not surprising, since the discrete set of hydrogenic functions is not a complete set. We could expect better agreement if we used different basis functions, such as generalized Laguerre polynomials with one exponential. The calculation of Smith *et al.*[14] is well over 0.5 eV below all other results, and should probably be reexamined.

In Table II, the energies of the eight lowest $^2P^o$ levels for He are listed. Their energies below the five doubly excited thresholds used in the calculation are also included. We see that only the lowest level lies below the $(2,2a)^1S^e$ state, and only one other (the one at 58.2 eV lies below the second-lowest doubly excited state. We feel that our method (and any other method which uses discrete bases) can treat definitively only those Feshbach resonances[19] which lie below the lowest doubly excited threshold included in the calculation. For this reason, the resonances quoted in this paper lying above the lowest $^2S^e$ threshold should be used with some caution. Keep in mind, though, that there must exist resonances in that region, and some (if not all) of the quoted levels will correspond to experimental reality.

It should be mentioned here that the threshold energies quoted in this paper are higher than those calculated in other papers by similar methods.[6,15] This is due to the fact that we have only included s, p, and d orbitals and $n = 2, 3, 4, 5$ states. A forthcoming paper on doubly excited states by Lipsky, Conneely, and Anania[15] will include all orbitals through h ($l = 5$), and some principal quantum numbers through $n = 10$. They report energy levels which are on the order of 0.02 eV lower than the doubly excited levels quoted here.

Once the formalism is set up for a given configuration (e.g., $^2P^o$) it is not hard to perform the same calculation for any Z. In Table III we report the results of such calculations for all nuclear charges from 1 to 10. All levels given in this table lie below the $(2s2p)^1P^o$ threshold for that system. Table IV gives the energies of the lowest doubly excited state for each of the configurations $^1S^e$, $^{1,3}P^o$, $^3P^e$, $^1D^o$ for every Z from 1 to 10. These are, of course, the five lowest thresholds below which the triply excited states are supposed to lie.

Similar calculations have been performed for the energy levels of $^2S^e$ triply excited states. The basis functions $\{\Phi_i\}$ used in this calculation contained the three-electron configurations built upon the following four doubly excited He targets:

$$(2,2a)^1S^e,\quad (2s2p)^{1,3}P^o,\quad \text{and}\quad (2p^2)^1D^e.$$

The lowest $^2S^e$ levels are tabulated in Table V.

Two $^2S^e$ triply excited states of He$^-$ are observed experimentally by Grissom *et al.*,[10] having energies around 59.4 and 58.79 eV, respectively. Our calculation, on the other hand, gives several levels in that energy range. We find one value at 59.61 eV corresponding to the 59.4 eV they report, but we have two levels, 58.71 and 58.79 eV, which could correspond to the one they report at 58.8 eV. Furthermore, we calculate one level at 58.07 eV, which is only 0.16 eV above the ^1S threshold. This level's existence may have been obscured by the presence of that threshold.

TABLE II. Lowest $^2P^o$ energy levels in He$^-$ as calculated using five two-electron target functions.

	Energy (a.u.)	Energy (eV)	Energy differences from the thresholds (eV) $(2,2a)\,^1S^e$	$(2s2p)\,^3P^o$	$(2p^2)\,^3P^e$	$(2p^2)\,^1D^e$	$(2s2p)\,^1P^o$
1	−0.795 217	57.3500	0.5630	1.0238	2.4230	2.6874	2.9322
2	−0.763 004	58.2265	···	0.1473	1.5465	1.8109	2.0557
3	−0.750 180	58.5754	···	···	1.1976	1.4620	1.7068
4	−0.736 239	58.9547	···	···	0.8183	1.0827	1.3275
5	−0.729 234	59.1453	···	···	0.6277	0.8921	1.1369
6	−0.711 747	59.6212	···	···	0.1518	0.4162	0.6610
7	−0.693 873	60.1075	···	···	···	···	0.1747
8	−0.688 598	60.2510	···	···	···	···	0.0312
Threshold energies (eV)			57.9130	58.3738	59.7730	60.0374	60.2822

TABLE III. Lowest $^2P^o$ energy levels for the He$^-$ isoelectronic sequence, expressed in a. u. below total ionization.

Z = 1	2	3	4	5	6	7	8	9	10
−0.116 612 [a]	−0.795 217	−2.237 332	−4.428 139	−7.369 360	−11.061 27	−15.503 78	−20.696 73	−26.640 02	−33.333 55
−0.112 564 [a]	−0.763 004	−1.992 823	−4.023 284	−6.827 824	−10.385 08	−14.694 15	−19.754 54	−25.565 87	−32.127 91
	−0.750 180	−1.977 296	−3.830 643	−6.285 765	−9.352 667	−13.031 33	−17.321 64	−22.223 46	−27.736 69
	−0.736 239	−1.957 597	−3.786 295	−6.216 370	−9.257 262	−12.910 16	−17.175 30	−22.052 60	−27.541 85
	−0.729 234	−1.930 839	−3.705 008	−6.094 926	−9.096 043	−12.708 92	−16.934 25	−21.774 39	−27.232 78
	−0.711 747	−1.924 614	−3.679 182	−6.050 923	−9.062 984	−12.687 40	−16.923 53	−21.768 85	−27.219 64
	−0.693 873	−1.906 205	−3.651 669	−6.004 509	−8.989 001	−12.585 76	−16.794 01	−21.613 81	−27.045 18
	−0.688 598	−1.863 538	−3.646 013	−5.978 168	−8.879 423	−12.448 87	−16.630 22	−21.423 54	−26.828 89
		−1.856 891	−3.619 558	−5.936 009	−8.846 830	−12.377 44	−16.548 73	−21.333 66	−26.730 93
		−1.853 743	−3.596 842	−5.913 426	−8.803 710	−12.254 51	−16.240 95	−20.789 27	−25.900 54
		−1.821 748	−3.564 308	−5.878 935	−8.776 966	−12.189 11	−16.162 02	−20.698 09	−25.797 68
		−1.800 661	−3.524 047	−5.859 969	−8.714 999	−12.107 95	−16.061 27	−20.576 76	−25.655 34
		−1.798 138	−3.504 641	−5.759 850	−8.569 285	−11.937 33	−15.866 60	−20.358 63	−25.414 10
		−1.790 594	−3.478 355	−5.718 603	−8.518 990	−11.881 58	−15.807 14	−20.295 87	−25.347 78
		−1.759 686	−3.443 124	−5.673 068	−8.458 004	−11.801 20	−15.705 46	−20.172 14	−25.201 94
		−1.745 911	−3.429 932	−5.661 267	−8.443 753	−11.778 27	−15.671 55	−20.129 58	−25.152 69
			−3.391 780	−5.622 610	−8.400 180	−11.726 34	−15.594 92	−20.000 64	−24.943 68
				−5.506 365	−8.289 198	−11.612 71	−15.474 83	−19.874 92	−24.812 98
				−5.406 162	−8.150 130	−11.456 15	−15.306 92	−19.698 43	−24.629 20
				−5.380 928	−8.122 296	−11.389 00	−15.193 63	−19.538 19	−24.423 79

[a] Above the $(2s2p)\,^1P^o$ threshold. These are used in the $1/Z$ perturbation theory fit.

TABLE IV. Doubly excited target thresholds for the He isoelectronic sequence for $Z=1$ to $Z=10$, expressed in a.u. below total ionization.

	Target threshold energies (a.u.)				
Z	$(2,2a)\,^1S^e$	$(2s2p)\,^3P^o$	$(2p^2)\,^3P^e$	$(2p^2)\,^1D^e$	$(2s2p)\,^1P^o$
1	−0.147 740	−0.141 791	−0.124 988	−0.127 623	−0.125 827
2	−0.774 522	−0.757 588	−0.706 166	−0.696 448	−0.687 454
3	−1.901 094	−1.873 643	−1.789 498	−1.758 493	−1.745 186
4	−3.527 836	−3.490 166	−3.373 959	−3.320 759	−3.302 136
5	−5.654 583	−5.606 933	−5.458 984	−5.383 758	−5.359 355
6	−8.281 589	−8.223 833	−8.044 310	−7.947 281	−7.916 888
7	−11.408 53	−11.340 81	−11.129 81	−11.011 14	−10.974 66
8	−15.035 50	−14.957 84	−14.715 42	−14.575 24	−14.532 61
9	−19.162 48	−19.074 90	−18.801 10	−18.639 50	−18.590 68
10	−23.789 48	−23.691 99	−23.386 84	−23.203 87	−23.148 85

Table VI is similar to Table III in that it contains the lowest $^2S^e$ triply excited states which lie below the $^1D^e$ threshold for each nuclear charge from 1 to 10.

The last set of levels we calculated were those for $^2D^e$, which were carried out only for He$^-$. Here, seven doubly excited target states were included. In addition to the five which were used in the $^2P^o$ calculation, we included the second lowest $^1S^e\,(2,2b)$ and $^1P^o\,(2,3b)$ states. Table VII indicates our value of 58.43 eV agrees reasonably well with experiment[8-10] and other calculations.[12-14] However, the experimental values all fall below the $^3P^o$ threshold at 58.36 eV, whereas all the theoretical calculations fall at or above that threshold, so the difference between theory and experiment is small but significant.

Table VIII contains the 13 lowest $^2D^e$ levels for He$^-$. Here we see that the two lowest levels (at 58.43 and 58.52 eV) are separated by less than 0.1 eV, so if the lowest resonance is below the $^3P^o$ threshold, then there could be another one right at that threshold.

There has been some experimental and theoretical interest in triply excited states in Li recently. In particular, Bruch *et al.*[22] have reported structures in electron emission from foil-excited states in Li which cannot be explained by doubly excited states. Our lowest $^2P^o$ state [taken from Table III and using Eq. (31c)] gives a value of 142.55 eV above the Li ground state, while our lowest $^2S^e$ state (Table VI) gives a value of 147.39 eV. Both states can autoionize to a $1s2l$ continuum, giving off an electron with energy of 80 to 86 eV. It is in this range that the otherwise unexplained resonant structures lie. Nicolaides[12] has calculated a value of 141.7 eV (misquoted as 140.7 in his paper) for the lowest $^2P^o$ state.

IV. Z DEPENDENCE FOR THE $(2s2p^2)\,^2S^e$, $(2s^22p)\,^2P^o$, AND $(2p^3)\,^2P^o$ LEVELS

It is of interest to study the dependence of the various energy levels on the charge of the nucleus. We have fitted the lowest $^2S^e$ level of Table VI and the two lowest $^2P^o$ levels of Table III to a perturbation theory expansion in $1/Z$,[23] retaining terms up to the order $1/Z^3$. From perturbation theory it can be shown that by scaling the coordinates of the electrons $(r_i \to r_i/Z)$ the energy E can be expressed as follows:

$$E(Z)=E_0+Z\langle\Phi_0|V|\Phi_0\rangle+A+B/Z+\cdots, \qquad (32)$$

where

$$H_0|\Phi_0\rangle=E_0|\Phi_0\rangle,$$

$$H_0=\sum_{i=1}^{3}\left(-\tfrac{1}{2}\nabla_i^2-\frac{Z}{r_i}\right),$$

TABLE V. Lowest $^2S^e$ energy levels for the He$^-$ as calculated using four two-electron target functions.

Energy (a.u.)	Energy (eV)	Energy differences from the thresholds (eV) $(2,2a)\,^1S^e$	$(2s2p)\,^3P^o$	$(2p^2)\,^1D^e$	$(2s2p)\,^1P^o$
−0.768 649	58.0729	...	0.3010	1.9646	2.2093
−0.745 258	58.7093	...	...	1.3281	1.5729
−0.742 416	58.7866	...	...	1.2508	1.4955
−0.712 023	59.6137	...	...	0.4238	0.6685
Threshold energies (eV)		57.9130	58.3738	60.0374	60.2822

TABLE VI. Lowest ${}^2S^e$ energy level for the He$^-$ isoelectronic sequence, expressed in a.u. below total ionization.

Z = 1	2	3	4	5	6	7	8	9	10
−0.118 193[a]	−0.768 649	−2.059 242	−4.155 947	−7.010 872	−10.618 43	−14.977 51	−20.087 58	−25.948 33	−32.559 57
	−0.745 258	−2.000 671	−3.856 790	−6.322 567	−9.399 70	−13.088 42	−17.388 64	−22.300 30	−27.823 30
	−0.742 416	−1.946 582	−3.739 861	−6.149 902	−9.170 64	−12.802 80	−17.046 85	−21.902 86	−27.370 75
	−0.712 023	−1.935 286	−3.693 539	−6.011 336	−8.963 03	−12.547 94	−16.747 06	−21.558 80	−26.982 78
		−1.876 317	−3.624 845	−5.963 069	−8.953 89	−12.345 78	−16.510 48	−21.287 50	−26.676 41
		−1.835 791	−3.593 361	−5.899 455	−8.791 74	−12.284 28	−16.277 12	−20.832 23	−25.950 24
		−1.801 004	−3.519 036	−5.848 232	−8.739 12	−12.138 56	−16.098 45	−20.621 00	−25.706 97
		−1.787 424	−3.473 394	−5.714 676	−8.509 08	−11.857 09	−15.764 32	−20.235 07	−25.270 41
			−3.426 092	−5.662 587	−8.446 49	−11.780 05	−15.669 59	−20.125 77	−25.147 24
			−3.413 836	−5.641 598	−8.420 60	−11.753 99	−15.633 37	−20.046 18	−24.994 24
				−5.403 891	−8.188 43	−11.494 67	−15.346 08	−19.739 80	−24.673 90
					−7.953 04	−11.224 87	−15.033 76	−19.379 21	−24.261 76
						−11.131 82	−14.926 97	−19.261 89	−24.135 85
								−18.850 43	−23.730 76

[a] Above the $(2s2p)\,{}^1P^o$ thresholds. This level is used in $1/Z$ perturbation theory fit.

TABLE VII. Position of $(2s2p^2)\,^2D^e$ resonance in He$^-$.

Experiment (eV)	Theory (eV)	Present calculation (eV)
58.23 ± 0.04 [a]	58.3 [e]	
58.2 ± 0.1 [b]	58.4 [f]	58.433
58.25 ± 0.05 [c]	58.3 [g]	
58.31 [d]		

[a] Reference 11.
[b] Reference 8.
[c] Reference 9.
[d] Reference 10.
[e] Reference 13.
[f] Reference 12.
[g] Reference 14.

and

$$V = \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\,.$$

The letters A and B involve matrix elements, which are independent of Z.

To apply the above analysis to the lowest $^2S^e$ energy level, we have taken

$$\bar{\Phi}_0 = \bar{\Phi}[(2s2p^2)\,^2S^e]\,,$$

which is a coupled the totally antisymmetrized three-electron product function. Now this function can be expressed in terms of the Φ_i's of Eq. (8) as follows:

$$\bar{\Phi}_0 = (1/\sqrt{3})[\Phi(2p^2\,^1S2s) - (1/\sqrt{2})\Phi(2s2p\,^1P2p) + \sqrt{\tfrac{3}{2}}\,\Phi(2s2p\,^3P2p)]\,.$$

We note that since $\bar{\Phi}_0$ is totally antisymmetric, we have

$$\langle\bar{\Phi}_0|V|\bar{\Phi}_0\rangle = 3\langle\bar{\Phi}_0|(1/r_{12})|\bar{\Phi}_0\rangle = 3\langle\bar{\Phi}_0|V_{12}|\bar{\Phi}_0\rangle$$

and

$$\begin{aligned}\langle\bar{\Phi}_0|V|\bar{\Phi}_0\rangle = {} & \langle\phi(2p^2\,^1S)|V_{12}|\phi(2p^2\,^1S)\rangle \\ & + \tfrac{1}{2}\langle\phi(2s2p\,^1P)|V_{12}|\phi(2s2p\,^1P)\rangle \\ & + \tfrac{3}{2}\langle\phi(2s2p\,^3P)|V_{12}|\phi(2s2p\,^3P)\rangle\,.\end{aligned}$$

The ϕ's are the same as those in Eq. (3b), with $Z = 1$. We use the values of two-electron matrix elements in the hydrogenic basis and get

$$\langle\bar{\Phi}_0|V|\bar{\Phi}_0\rangle \equiv \lambda = 0.511\,718\,8 \tag{33a}$$

and

$$E_0(2p^2\,^1S2s) = -\tfrac{1}{2}Z^2(\tfrac{1}{4}+\tfrac{1}{4}+\tfrac{1}{4}) = -\tfrac{3}{8}Z^2 \text{ (a.u.)}. \tag{33b}$$

The expression $E(Z) + \frac{3}{8}Z^2 - 0.511\,718\,8Z$, where $E(Z)$ is taken from the first row of Table VI, is plotted against $1/Z$ in Fig. 2. The plot shows that the linear fit is good for $Z > 5$.

To extend this analysis to the lowest two $^2P^o$ levels, we note that in this case, there are two degenerate unperturbed levels:

$$\bar{\Phi}_{01} \equiv \bar{\Phi}_{01}[(2s^2\,2p)\,^2P^o]\,,$$

$$\bar{\Phi}_{02} \equiv \bar{\Phi}_{02}[(2p^3)\,^2P^o]\,.$$

$\bar{\Phi}_{01}$ and $\bar{\Phi}_{02}$ can be written as

$$\bar{\Phi}_{01} = (1/\sqrt{3})[\Phi(2s^2\,^1S2p) - (1/\sqrt{2})\Phi(2s2p\,^1P2s) - \sqrt{\tfrac{3}{2}}\,\Phi(2s2p\,^3P2s)]\,,$$

$$\bar{\Phi}_{02} = \sqrt{\tfrac{1}{3}}\,[\sqrt{\tfrac{2}{3}}\,\Phi(2p^2\,^1S2p) - \sqrt{\tfrac{3}{2}}\,\Phi(2p^2\,^3P2p) - \sqrt{\tfrac{5}{6}}\,\Phi(2p^2\,^1D2p)]\,.$$

Following the procedure of degenerate perturbation theory,[24] we have to diagonalize the matrix:

$$\begin{bmatrix}\langle 2s^2\,^1S|V_{12}|2s^2\,^1S\rangle & \langle 2s^2\,^1S|V_{12}|2p^2\,^1S\rangle \\ \langle 2p^2\,^1S|V_{12}|2s^2\,^1S\rangle & \langle 2p^2\,^1S|V_{12}|2p^2\,^1S\rangle\end{bmatrix}.$$

TABLE VIII. Lowest $^2D^e$ energy levels in He$^-$ as calculated using seven two-electron target functions.

Energy (a.u.)	Energy (eV)	Energy differences from the thresholds (eV) $(2,2a)\,^1S^e$	$(2s2p)\,^3P^o$	$(2p^2)\,^3P^e$	$(2p^2)\,^1D^e$	$(2s2p)\,^1P^o$	$(2,2b)\,^1S^e$	$(2,3b)\,^3P^o$
−0.755 416	58.4329	···	···	1.3401	1.6045	1.8492	3.8456	4.3309
−0.752 229	58.5196	···	···	1.2534	1.5178	1.7625	3.7589	4.2442
−0.741 436	58.8133	···	···	0.9597	1.2241	1.4688	3.4652	3.9505
−0.705 968	59.7784	···	···	···	0.2591	0.5038	2.5001	2.9854
−0.694 605	60.0876	···	···	···	···	0.1946	2.1909	2.6762
−0.687 960	60.2684	···	···	···	···	0.0138	2.0101	2.4954
−0.683 837	60.3806	···	···	···	···	···	1.8979	2.3832
−0.679 340	60.5029	···	···	···	···	···	1.7756	2.2609
−0.671 432	60.7181	···	···	···	···	···	1.5604	2.0457
−0.657 672	61.0925	···	···	···	···	···	1.1860	1.6713
−0.640 338	61.5642	···	···	···	···	···	0.7143	1.1996
−0.622 390	62.0525	···	···	···	···	···	0.2260	0.7113
−0.617 703	62.1801	···	···	···	···	···	0.0984	0.5837
Threshold energies (eV)		57.9130	58.3738	59.7730	60.0374	60.2822	62.2785	62.7638

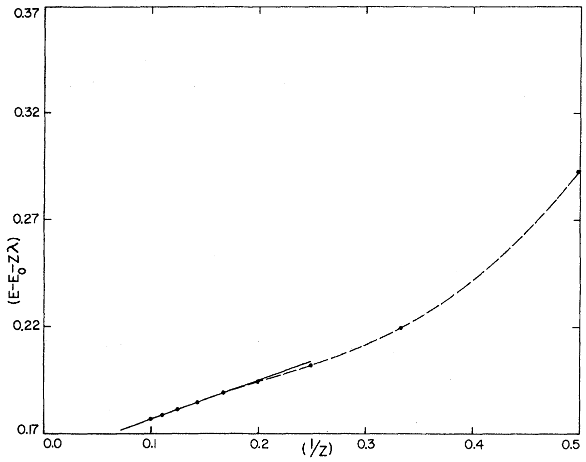

FIG. 2. $1/Z$ expansion to the lowest ${}^2S^e$ energy level, where the unperturbed state is $(2s2p^2)^2S^e$.

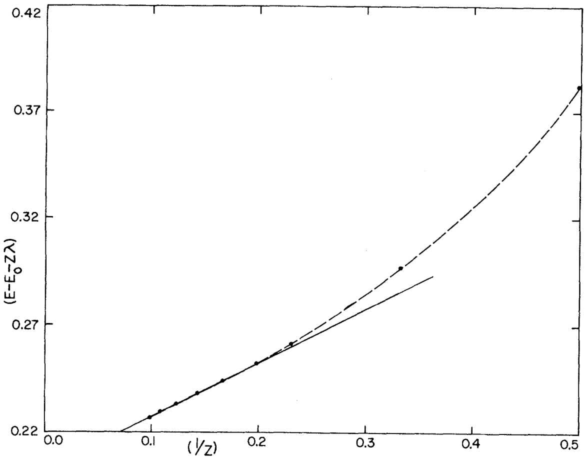

FIG. 4. $1/Z$ perturbation theory fit to the second lowest ${}^2P^o$ level.

The two eigenvalues obtained are

$$\lambda_1 = 0.430\,33, \quad \lambda_2 = 0.5599. \tag{33c}$$

The smaller value corresponds to the lowest ${}^2P^o$ energy level, and λ_2 corresponds to the next lowest level, while E_0 is the same for both and the same as Eq. (33b). The expressions $E_i(Z) + 3Z^2/8 - \lambda_i Z$, for $i = 1$ and 2, are plotted as functions of $1/Z$ in Figs. 3 and 4, respectively. $E_1(Z)$ and $E_2(Z)$ come from the first two rows of Table III.

V. FURTHER DISCUSSION

A. On the linear independence of Ψ_i's and on their orthogonality to lower states

According to the development of Sec. II, the X matrix [Eq. (4)] gives the overlaps among the functions $\{\Psi_i\}$. These functions (and equivalently $\{\overline{\Psi}_i\}$) form a basis set in the physical space. The physical space is a subspace of the full configuration space spanned by the Φ_i's. The dimensions of the subspace which we use here are determined by the number of doubly excited targets and the number of one-electron functions which are coupled to each of these targets. Now, to do the calculation of a triply excited state by our method, we have chosen a few of the low-lying doubly excited targets (see Sec. III for details). The basis functions $\{\Psi_i\}$ thus constructed will normally be linearly independent, as is manifested mathematically when the X matrix has no zero eigenvalues. But the formalism also provides a test of linear independence for the basis set $\{\Psi_i\}$ in the physical space. That means if we had initially constructed a set which was not linearly independent, then some of the eigenvalues of X would be zero, and by throwing away the corresponding eigenvectors of X, one could obtain a linearly independent, orthonormal basis set $\{\overline{\Psi}_i\}$ as described in Sec. II. In such a case, this set would span the appropriately reduced subspace of physical space.

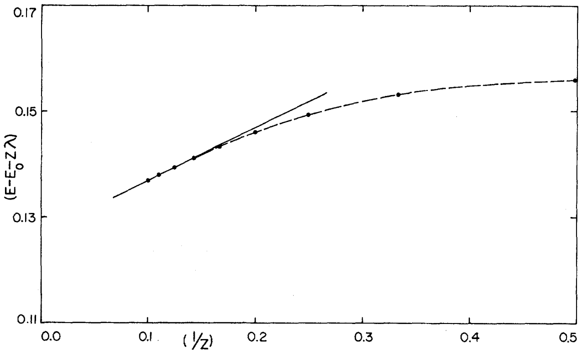

FIG. 3. $1/Z$ expansion of the lowest ${}^2P^o$ level.

Another point on which we would like to comment here is the orthogonality of the functions $\{\Psi_i\}$ to lower-lying states of the same symmetry. As mentioned in Sec. I, these functions are approximately orthogonal to all the states of the same symmetry, i.e., to the low-lying discrete states (singly and doubly excited), and also to the states lying in one- and two-electron continua. This is so because these functions are made up of products of various doubly excited states of the target with single-particle hydrogenic states. Now, the doubly excited states of the two-electron target are orthogonal to all the singly excited eigenstates (including the ground state) of the two-electron Hamiltonian, and the singly excited one-electron states of the additional electron are also mutually orthogonal as well as orthogonal to (1s) (the ground-state orbital). Therefore, the wave function of the triply excited state in the Ψ_i basis constructed by our method is approximately orthogonal to all the low-lying singly excited and doubly excited states of the same symmetry. The asymptotic behavior of the continuum states in the one- and two-electron continua is different from the asymptotic behavior of a triply excited state, which decreases exponentially as a function of the coordinates of any of the three electrons. So all the continuum states are also orthogonal to the wave function of the triply excited states.

B. Calculation of $(2s^2\,2P)\,^2P^o$ level using the full Φ_i basis set

We would like to comment here on employing the full basis set $\{\Phi_i\}$ for the expansion of the wave function of a triply excited state. In Sec. III we described the calculation of triply excited levels using CI wave functions for the low-lying doubly excited two-electron targets. To study in some detail the differences between the two approaches, we have performed the calculation of the energy of the lowest $^2P^o$ level, $(2s^2\,2p)$, in He$^-$ using the full Φ_i basis. That is, we diagonalized the total three-electron Hamiltonian matrix

$$\bar{\mathcal{H}} = AHA \tag{34}$$

evaluated in the Φ_i basis consisting of all the three-electron configurations up to a certain maximum value of n_i and l_i $(i=1,3)$, From the formalism developed in Sec. II C, this could be accomplished either by calculating the Hamiltonian matrix with respect to the eigenstates of A belonging only to nonzero eigenvalues or equivalently by calculating the matrix,

$$\mathcal{H}' = aHa^T \tag{35}$$

with some known a.

We now consider the Hamiltonian matrix $\mathcal{H}$ evaluated in the $\bar{\Psi}_i$ basis [Eq. (15), Sec. II B] which includes all the doubly excited states of He lying below the various thresholds of He$^+$, with nl ranging from 2s up to $n_i^{\max} l_i^{\max}$ and having symmetries $^{1,3}S^e$, $^{1,3}P^o$, $^{1,3}P^e$, $^{1,3}D^e$, $^{1,3}D^o$, and $^{1,3}F^o$. Since α in this case is square and unitary and the X matrix is given by Eq. (11):

$$X = \alpha A \alpha^T ,$$

where X and α are of the same order as the A matrix $(m \times m)$; therefore X is a projection operator just like A with the eigenvalues 0 and 1 only. Now the Hamiltonian matrix $\mathcal{H}$ has the form:

$$\mathcal{H} = \alpha A H A \alpha^T ,$$

which has the same eigenvalues as

$$\bar{\mathcal{H}} = AHA ,$$

and thus the same nonzero eigenvalues as $\mathcal{H}'$. We have then shown that using the full Φ_i basis (i.e., employing the straightforward CI expansion for the wave function of a triply excited state) is for-

TABLE IX. Energy of lowest $^2P^o$ state in He$^-$ using different basis sets. The energy entries are in a.u.; these are also given within parentheses in eV.

Configurations included	$n^{\max}$ 3	4	5
ssp (No constraints)	−0.754 915 43 (58.4466)	−0.758 350 65 (58.3531)	−0.759 145 13 (58.3315)
ssp (3-TDM targets, $^1S^e$ and $^{1,3}P^o$)	−0.754 382 40 (58.4611)	−0.757 819 46 (58.3676)	−0.758 813 70 (58.3405)
ssp, p^3 (No constraints)	−0.779 996 49 (57.7641)	−0.781 496 42 (57.7233)	...
ssp, p^3 (5-TDM targets $^1S^e$, $^{1,3}P^o$, $^3P^e$, and $^1D^e$)	−0.779 019 17 (57.7907)	−0.779 931 54 (57.7659)	−0.781 008 56 (57.7366)
All [a] (No constraints)	−0.795 636 64 (57.3385)	−0.796 880 50 (57.3047)	...
All [a] (5-TDM targets, $^1S^e$, $^{1,3}P^o$, $^3P^e$, and $^1D^e$)	−0.793 559 21 (57.3951)	−0.794 690 74 (57.3643)	−0.795 216 74 (57.3500)

[a] The three-electron configurations used for these calculations are (n_1s, n_2s, n_3p), (n_1p, n_2p, n_3p), (n_1s, n_2p, n_3d), (n_1p, n_2d, n_3d), where $2 \le n_1, n_2, n_3 \le n^{\max}$.

TABLE X. Calculated energy of lowest $^2P^o$ level in He$^-$ with increasing number of target states.

Energy of $(2s^22p)\,^2P^o$ level in He$^-$ (eV)	$(2,2a)\,^1S^e$	Energy differences from target thresholds (eV) $(2s2p)\,^3P^o$	$(2p^2)\,^3P^e$	$(2p^2)\,^1D^e$	$(2s2p)\,^1P^o$
58.1540	a	b	b	b	b
57.7823	0.1307	b	b	b	2.4999
57.4910	0.4220	0.8828	b	b	2.7912
57.3831	0.5299	0.9907	2.3899	b	2.8991
57.3500	0.5630	1.0238	2.4230	2.6874	2.9322
Threshold energies (eV)	57.9130	58.3738	59.7730	60.0374	60.2822

[a] Indicates that the energy level is above the particular threshold.
[b] Indicates that the particular target was not included in the calculation.

mally equivalent to expanding this wave function in a linear combination of the products of all the doubly excited CI target functions with various one-electron functions. For comparison, we list in Table IX the results of the calculation for the energy of $(2s^2\,2p)\,^2P^o$ state in He$^-$ with CI functions for the lowest doubly excited two-electron targets, and also without them (i.e., using full $\overline{\Phi}$ basis) for different values of $n_i^{\max}$ and $l_i^{\max}$ ($3 \leq n_i^{\max} \leq 5$, $1 \leq l_i^{\max} \leq 2$).

We observe from Table IX that the difference between calculations using doubly excited targets and those which use the full Φ basis (i.e., have no constraints) is less than 0.06 eV. This is rather surprising, since we had expected that the latter calculations would have yielded much lower energy values, perhaps even lower than experiment, and comparable to the calculation of Smith *et al.*[14] Since this did not happen, we must conclude that either we did not include enough radial configurations (including all $n=5$ states would have required the diagonalization of a 340×340 matrix—an impossibility on our computer system) or orthogonality to the $1s$ orbital is all that is necessary to define triply excited states. In other words, a projection operator can be constructed (a direct extension of the Q of Hahn, O'Malley, and Spruch[25] for two electrons) which projects out the ground state of the one-electron system.

Of course, a calculation which includes several two-electron CI functions will yield lower energies than equivalent calculations using fewer CI functions. Table X shows the results of calculations where one to five target states were included. First, a calculation using only the lowest $^1S^e$ state yielded an energy of 58.1540 eV for the lowest $^2P^o$ triply excited state. Next, two target states were included, the lowest $^1S^e$ and the lowest $^1P^o$, giving an energy of 57.7823 eV. Then, successively, the lowest $^3P^o$, $^3P^e$, and $^1D^e$ states were included, giving energies of 57.4910, 57.3831, and 57.3500 eV, respectively. Naturally, if more and more states were added, the calculated energies for the triply excited states would approach the eigenvalues of $\overline{\mathcal{H}}$ [Eq. (34)] or $\mathcal{H}'$ [Eq. (35)]. But, after some point, states would be added which are poor approximations to their respective doubly excited targets, thereby, presumably losing the orthogonality to the singly excited states.

C. Relation with close-coupling method

Here we discuss some of the points relating our method of calculation for triply excited levels with the close-coupling procedure. In the close-coupling procedure for electron-atom scattering the wave function is expanded in a linear combination of products of target eigenfunctions, ψ_t with some unknown functions for the additional electron, $F_\mu(r)$. The unknown functions F_μ's satisfy second-order integrodifferential equations obtained from Kohn's variational principle.[25] In the CI method, on the other hand, known functions R_{nl} are used for the additional electron, and the N independent expansion coefficients are chosen such that the energy is minimized, which is equivalent to diagonalizing the Hamiltonian matrix. Thus, the configuration-interaction method is equivalent to a close-coupling procedure involving closed channels only. Our approach, using CI target eigenfunctions for the doubly excited target states is better than the close-coupling approximation, in the sense that we can use more accurate ψ_t's. But the close-coupling approximation is better in the respect that the functions F_μ are more accurately and efficiently determined, as these are the actual solutions to the differential equations describing the multichannel scattering.

To achieve the same accuracy as that of a close-coupling calculation, we would have to include many more hydrogenic single-particle orbitals for the additional electron. We can expect to speed up the convergence if we use as R_{nl}'s, generalized Laguerre functions (of which Sturmians are perhaps the best known set) in the place of hydrogenic radial functions. Because these functions are more compact and tightly bound than the hydrogenic, one can achieve some of the advantages of the variationally determined F_μ's for the low-lying multiply excited states. Also the generalized Laguerre functions, being a complete set, represent well the contributions from the continuum. However, the hydrogenic radial functions are better suited to describe the higher members of Rydberg series of triply excited states since the Laguerre functions are more tightly bound, and more of them will be required to describe an electron of relatively high quantum number.

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APPENDIX A. DERIVATION OF THE MATRIX REPRESENTATION OF A IN THE Φ_i BASIS

The antisymmetrization operator for $N+1$ particles, A_{N+1} can be written in terms of that for N particles, A_N, as follows:

$$A_{N+1}=\frac{1}{(N+1)!}\sum_p(-1)^p P_p$$

$$=\frac{1}{N+1}(1-P_{1,N+1}-P_{2,N+1}\cdots-P_{N,N+1})A_N\ ,$$

where $P_{i,N+1}$ ($i=1, N$) denotes the interchange operator for the pair of particles i and $N+1$.

If we use as basis functions Φ's which are antisymmetric in the first N particles but not in the $(N+1)$ st, we have

$$(A_{N+1})_{ij}=\langle\Phi_i|A_{N+1}|\Phi_j\rangle$$

$$=\langle\Phi_i|(1-P_{1,N+1}-P_{2,N+1}\cdots-P_{N,N+1})|\Phi_j\rangle/(N+1)\ ,$$

since, by definition of the Φ's,

$$A_N\Phi_j(1,2,\ldots,N;N+1)=\Phi_j\ .$$

Also, since

$$P_{i,N+1}=P_{Ni}P_{N,N+1}P_{Ni}\quad(1\leqslant i<N)$$

and

$$P_{Ni}\Phi_j(1,\ldots,i,\ldots,N;N+1)=\Phi_j(1,\ldots,N,\ldots,i;N+1)=-\Phi_j(1,\ldots,i,\ldots,N;N+1)\ ,$$

we have

$$\langle\Phi_i|P_{i,N+1}|\Phi_j\rangle=\langle\Phi_i|P_{N,N+1}|\Phi_j\rangle\ .$$

So

$$A_{ij}=[1/(N+1)](\delta_{ij}-N\langle\Phi_i|P_{N,N+1}|\Phi_j\rangle) \qquad \text{(A1)}$$

or, in matrix form,

$$A=[1/(N+1)](I-NP_{N,N+1})\ . \qquad \text{(A2)}$$

In particular, for $N=3$,

$$A_{ij}=\langle\Phi_i|\tfrac{1}{3}(1-2P_{23})|\Phi_j\rangle=\tfrac{1}{3}[\delta_{ij}-2\langle\Phi_i|P_{23}|\Phi_j\rangle] \qquad \text{(A3a)}$$

or

$$A=\tfrac{1}{3}[I-2P_{23}]\ . \qquad \text{(A3b)}$$

Note that this equation is *not* a general operator equation, since it does not hold for the evaluation of the matrix elements between states which do not satisfy Eq. (17). One may ask the question, then, if there is an operator p for which

$$A=\tfrac{1}{3}(I-2p) \qquad \text{(A4a)}$$

is always true. The answer is yes, namely

$$p=\frac{1+P_{12}}{4}+\left(\frac{1-P_{12}}{2}\right)P_{23}\left(\frac{1-P_{12}}{2}\right)\ . \qquad \text{(A4b)}$$

Equations (A4a) and (A4b) together present an identity for A

$$\langle\Phi_i|p|\Phi_j\rangle=\langle\Phi_i|P_{23}|\Phi_j\rangle\ .$$

As a result of the above we note that A can be used interchangeably with its matrix representation A_{ij}, but P_{23} cannot. We also know that A (and therefore P_{23} in the Φ basis) commutes with total $\vec{L}$ and $\vec{S}$; so we can write that

$$A=A(L,M_L,S,M_S)$$

and

$$P_{23}=P_{23}(L,M_L,S,M_S)\ .$$

The functions Φ_i and Φ_j are defined by Eq. (8) and can be written as (the quantum numbers associated with subscript j are denoted by primes):

$$\Phi_i(1,2;3)=N(n_1,l_1,n_2,l_2)\times[\phi(1,2,3|n_1l_1,n_2l_2,L_{12},S_{12},n_3l_3,L,S)-\phi(2,1,3|n_1l_1,n_2l_2,L_{12},S_{12},n_3l_3,L,S)]$$

$$\equiv N[\phi(1,2,3)-\phi(2,1,3)]\ .$$

Here

$$N(n_1, l_1, n_2, l_2) = \frac{1}{\sqrt{2} + (2 - \sqrt{2})\,\delta(n_1 n_2)\,\delta(l_1 l_2)} \tag{A5}$$

is the normalization constant and

$$\phi(1,2,3) = R_{n_1 l_1}(1)\,R_{n_2 l_2}(2)\,R_{n_3 l_3}(3) \times [\mathcal{Y}^{M_{12}}_{L_{12} l_1 l_2}(\hat{1},\hat{2})\,\chi^{\mu_{12}}_{S_{12}}\,Y^{m_3}_{l_3}(\hat{3})\,\chi^{\mu}_{1/2}]^{MM_S}_{LS}\,. \tag{A6}$$

Note that this ϕ is *not* antisymmetric in the interchange of any two particles.

Upon taking the scalar product $\langle\Phi_i|P_{23}|\Phi_j\rangle$, four terms appear. The first term is

$$M_1 = \langle\phi(1,2,3)|P_{23}|\,\phi'(1,2,3)\rangle$$
$$= \langle\phi(1,2,3)|\,\phi'(1,3,2)\rangle\ .$$

It can be shown that $\phi'(1,3,2)$ can be written in terms of the functions $\phi'(1,2,3)$ by carrying out a change of coupling transformation.[20] Therefore, we have

$$\phi'(1,3,2) \equiv \phi(1,3,2\,|\,n_1' l_1', n_2' l_2', L_{12}', S_{12}', n_3' l_3', L, S)$$
$$= \sum_{L_{13}' S_{13}'} \langle l_1' l_2'(L_{12}') l_3'; L\,|\,l_1' l_3'(L_{13}') l_2'; L\rangle \langle \tfrac{1}{2}\tfrac{1}{2}(S_{12}')\tfrac{1}{2}; S\,|\,\tfrac{1}{2}\tfrac{1}{2}(S_{13}')\tfrac{1}{2}; S\rangle\,\phi'(1,2,3)\ .$$

where

$$\langle l_1' l_2'(L_{12}') l_3'; L\,|\,l_1' l_3'(L_{13}') l_2'; L\rangle \langle \tfrac{1}{2}\tfrac{1}{2}(S_{12}')\tfrac{1}{2}; S\ \tfrac{1}{2}\tfrac{1}{2}(S_{13}')\tfrac{1}{2}; S\rangle = (-1)^{l_1'+l_2'+l_3'+L}(-1)^{S+1/2}(-1)^{l_3'+l_2'+L_{12}'+L_{13}'}(-1)^{S_{12}'+S_{13}'}$$
$$\times[L_{12}'][S_{12}'][L_{13}'][S_{13}']$$
$$\times W(l_1' l_3' l_2' L; L_{13}' L_{12}')\,W(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}S; S_{13}' S_{12}')\ .$$

Finally, the first term is

$$M_1 = \langle\phi_1(1,2,3)|\,\phi_1'(1,3,2)\rangle$$
$$= (-1)^{L_{12}+S_{12}+L_{12}'+S_{12}'}(-1)^{l_1+L}(-1)^{S+1/2}\times[L_{12}][S_{12}][S_{12}'][L_{12}']$$
$$\times\delta(n_1,n_1')\,\delta(l_1,l_1')\,\delta(n_2,n_3')\,\delta(l_2,l_3')\,\delta(n_3,n_2')\,\delta(l_3,l_2')\,W(l_1 l_2 l_3 L; L_{12} L_{12}')\,W(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}S; S_{12} S_{12}')\ . \tag{A7}$$

Here W is a Racah coefficient as defined in Rose.[17] Similarly, the second term is

$$M_2 = -\langle\phi(2,1,3)|P_{23}|\,\phi'(1,2,3)\rangle$$
$$= -\langle\phi(1,2,3)|\,\phi'(2,3,1)\rangle$$
$$= (-1)^{L_{12}+S_{12}}(-1)^{l_3+L}(-1)^{S+1/2}\times[L_{12}][S_{12}][L_{12}'][S_{12}']\,\delta(n_1 n_2')\,\delta(l_1 l_2')\,\delta(n_2 n_3')\,\delta(l_2 l_3')\,\delta(n_3 n_1')\,\delta(l_3 l_1')$$
$$\times W(l_1 l_2 l_3 L; L_{12} L_{12}')\,W(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}S; S_{12} S_{12}')\ . \tag{A8}$$

The third term is given by

$$M_3 = -\langle\phi'(1,2,3)|P_{23}|\,\phi(2,1,3)\rangle$$
$$= -\langle\phi(1,2,3)|\,\phi'(3,1,2)\rangle$$
$$= (-1)^{L_{12}'+S_{12}'}(-1)^{l_1+L}(-1)^{S+1/2}\times[L_{12}][L_{12}'][S_{12}][S_{12}']\delta(n_1 n_3')\delta(l_1 l_3')\delta(n_2 n_1')\delta(l_2 l_1')\delta(n_3 n_2')\delta(l_3 l_2')$$
$$\times W(l_2 l_1 l_3 L; L_{12} L_{12}')W(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}S; S_{12} S_{12}')\,. \tag{A8}$$

The fourth term is given by

$$M_4 = \langle\phi'(2,1,3)|P_{23}|\,\phi(2,1,3)\rangle$$
$$= \langle\phi(1,2,3)|\,\phi'(3,2,1)\rangle$$
$$= (-1)^{l_1+l_2+l_3+L}(-1)^{S+1/2}\times[L_{12}][S_{12}][L_{12}'][S_{12}']\delta(n_1 n_3')\delta(l_1 l_3')\delta(n_2 n_2')\delta(l_2 l_2')\delta(n_3 n_1')\delta(l_3 l_1')$$
$$\times W(l_2 l_1 l_3 L; L_{12} L_{12}')W(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}S; S_{12} S_{12}')\,. \tag{A9}$$

The notation $[L_{12}]$ etc. stands for

$$[L_{12}] = (2L_{12}+1)^{1/2}\ .$$

The final expression for A_{ij}, Eq. (A3), will, in general, be a sum of the above four terms plus a diagonal term whenever it is present; i.e.,

$$A_{ij} = \tfrac{1}{3}\delta_{ij} - \tfrac{2}{3}N_i N_j[M_1 + M_2 + M_3 + M_4]\,. \tag{A10}$$

APPENDIX B. EVALUATION OF TWO a MATRICES

Example 1

The matrix A as evaluated by the above procedure has already been given in Eq. (9) of Sec. II B with respect to the basis functions Φ_1, Φ_2 and Φ_3; that is,

$$A=\tfrac{1}{3}\begin{bmatrix} 1 & -1/\sqrt{2} & -\sqrt{\tfrac{3}{2}} \\ -1/\sqrt{2} & \tfrac{1}{2} & \sqrt{3}/2 \\ -\sqrt{\tfrac{3}{2}} & \sqrt{3}/2 & \tfrac{3}{2} \end{bmatrix}. \tag{B1}$$

The functions $A\Phi_1$, $A\Phi_2$, and $A\Phi_3$ are all proportional to each other in this case, and only one totally antisymmetric function ($\bar{\Phi}$) can be constructed from them. The a matrix, therefore, is of order (1×3), and from Eq. (20) of Sec. II C we have

$$\bar{\Phi}=\sum_{i=1}^{3} a_i\Phi_i\,. \tag{B2}$$

Also,

$$A\Phi_i = a_i\bar{\Phi} \quad (i=1,3) \tag{B3}$$

with the matrix a having the property

$$aa^T=I\,,\quad a^Ta=A\,.$$

As there is only one $\bar{\Phi}$, a is unique to within ± 1 and is given by

$$[a]=(1/\sqrt{3})[1 \;\; -1/\sqrt{2} \;\; -\sqrt{\tfrac{3}{2}}\,]\,. \tag{B4}$$

Example 2

Consider the following A matrix:

$$A=\tfrac{1}{3}\begin{bmatrix} 1 & 0 & -\tfrac{1}{2} & -\sqrt{3}/2 & -\tfrac{1}{2} & -\sqrt{3}/2 \\ 0 & 1 & -\sqrt{3}/2 & \tfrac{1}{2} & \sqrt{3}/2 & -\tfrac{1}{2} \\ -\sqrt{3}/2 & -\sqrt{3}/2 & 1 & 0 & -\tfrac{1}{2} & \sqrt{3}/2 \\ -\sqrt{3}/2 & \tfrac{1}{2} & 0 & 1 & \sqrt{3}/2 & \tfrac{1}{2} \\ -\tfrac{1}{2} & \sqrt{3}/2 & -\tfrac{1}{2} & \sqrt{3}/2 & 1 & 0 \\ -\sqrt{3}/2 & -\tfrac{1}{2} & \sqrt{3}/2 & \tfrac{1}{2} & 0 & 1 \end{bmatrix}. \tag{B5}$$

The above representation of A has been obtained with respect to the basis functions Φ_i ($i=1,6$), as defined below:

$$\Phi_{1,2}=\Phi(n_1sn_2s^{1,3}Sn_3p\,{}^2P^0)\,,$$

$$\Phi_{3,4}=\Phi(n_1sn_3p^{1,3}Pn_2s\,{}^2P^0)\,,$$

$$\Phi_{5,6}=\Phi(n_2sn_3p^{1,3}Pn_1s\,{}^2P^0)\,,\quad n_1\neq n_2\,.$$

We note here that the functions $A\Phi_1$ and $A\Phi_2$ are orthogonal to each other but are not normalized. Also the remaining functions, $A\Phi_3$, $A\Phi_4$, $A\Phi_5$, and $A\Phi_6$, can be represented as different linear combinations of $A\Phi_1$ and $A\Phi_2$. So if we construct a pair of orthonormal functions given by Φ_1,Φ_2, then we have [analogous to Eqs. (B1) and (B2)]

$$\bar{\Phi}_i=\sum_{j=1}^{6} a_{ij}\Phi_j \quad (i=1,2)\,, \tag{B6}$$

$$A\Phi_i=\sum_{j=1}^{2}(a^T)_{ij}\bar{\Phi}_j=\sum_{j=1}^{2}a_{ji}\bar{\Phi}_j \quad (i=1,6) \tag{B7}$$

and the a matrix satisfying the property

$$aa^T=I\,,\quad a^Ta=A\,.$$

We find that such an a matrix is given by

$$a=\frac{1}{\sqrt{3}}\begin{bmatrix} 1 & 0 & -\tfrac{1}{2} & -\sqrt{3}/2 & -\tfrac{1}{2} & -\sqrt{3}/2 \\ 0 & 1 & -\sqrt{3}/2 & \tfrac{1}{2} & \sqrt{3}/2 & -\tfrac{1}{2} \end{bmatrix}. \tag{B8}$$

The above examples lead us to a general statement of how one might get an a matrix directly from the A matrix. First of all, if we select a particular Φ_i and antisymmetrize it, we get

$$A\Phi_i=N_i\bar{\Phi}_i\,, \tag{B9}$$

where $\bar{\Phi}_i$ is a totally antisymmetric function of unit length. With the help of Eqs. (B6) and (B7), one can write

$$A_{ij}=N_ia_{ij} \quad (j=1,m)\,. \tag{B10}$$

This equation says that the ith column of A is proportional to one column of an acceptable a matrix. In example 1 all three columns of A are proportional to a [Eq. (B3)]. Now suppose that for some $k\neq i$, we have

$$A_{ik}=0\,, \tag{B11}$$

then

$$\begin{aligned} A_{ik} &= (A^2)_{ik} \quad (\text{since } A^2 = A) \\ &= \sum_j A_{ij} A_{jk} \\ &= \sum_j A_{ij} A_{kj} \\ &= 0 \,. \end{aligned}$$

This equation says that columns i and k are mutually orthogonal. Therefore the kth column can form another column of a. In example 2, we have three such zero pairs, $[(i,k) = (1,2), (3,4), (5,6)]$, allowing us to write down directly three different acceptable a's. Equation (B6) is the case for $(i,k) = (1,2)$. So, in those cases where there are as many mutually orthogonal (rows) columns in the A matrix as the dimension n of the subspace spanned by the eigenvectors of A, an a can easily be found by inspection.

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