J-matrix calculation of electron-helium *S*-wave scattering

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The J-matrix approach to electron-atom scattering is revised by merging it with the Fano's multiconfiguration interaction matrix elements [U. Fano, Phys. Rev. **140**, A67 (1965)]. The revised method is then applied to the S-wave model of the e-He scattering problem demonstrating remarkable computational efficiency and accuracy. In particular, the method is in complete agreement with the convergent-close-coupling elastic, $2^{1,3}S$ excitation and single ionization cross sections for impact energies in the range 0.1–1000 eV. The S-wave resonance structures in the elastic and $2^{1,3}S$ excitation cross sections are highlighted.

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I. INTRODUCTION

It has been known since at least 1994 that the J-matrix (JM) approach [1–3] to electron-atom scattering is comparable in accuracy to other scattering methods for elastic and excitation processes [4–6]. Most recently, it was demonstrated that the JM method is also capable of describing ionization processes when applied to the S-wave model of e-H scattering problem [7]. Encouraged by this success on the well-researched and arguably completely solved e-H model problem, we now proceed to the more complicated S-wave model of e-He scattering, with the goal of solving the ionization-with-excitation and double-ionization problems.

The step from e-H to e-He scattering is not trivial as the complexity of the problem increases from a three-body to a four-body problem. While the e-H model remains an important test bed of any new or past scattering methods [4,8–13], the focus of current state-of-the-art *ab initio* computational methods has shifted to the model of e-He scattering [14–21]. The presented here extension of the JM method combines the strengths of the R-matrix [22] and the convergent-close-coupling (CCC) [23] methods by efficiently obtaining results on a fine energy mesh and allowing the usage of large Laguerre expansion sets, respectively.

The S-wave model implies that only states with zero orbital angular momentum are retained in the calculation. This brings to the fore the complexities associated with treating the infinite discrete target spectrum, the target continuum, and the long-ranged nature of the Coulomb potential. In particular, the primary complexity of Coulomb few-body problems is retained as it is known that the S-wave elastic scattering cross section dominates over higher partial waves at the challenging region of low energies.

In the case of e-He scattering, the model can be further simplified by ensuring that all (two-electron) target states have the "inner" electron described by the He^+ $1s$ orbital, subject to appropriate symmetrization. We refer to this as the frozen-core approximation, and it is ideal for the present "proof-of-principle" calculations for the dominant one-electron excitation and single-ionization processes. However, when considering ionization-plus-excitation or double-ionization processes, this approximation will need to be removed, but how to correctly formulate such processes remains problematic for any theory.

The presented JM results are calculated using Java programming language, which is freely available for MS Windows, Mac OSX, and many versions of Linux or Unix. See [24] for information on availability of the source code used in this paper.

II. THEORY

A. Many-electron atomic systems

The focus of this study is the S-wave model of electron-helium (e-He) nonrelativistic collision with zero total angular momentum [20,21]. In a general case of an atomic system with the total number of electrons a and the nuclear charge Z, the S-wave term of the total Hamiltonian becomes

$$H_a = \sum_{b=1}^{a} h_b + \sum_{b=1}^{a}\sum_{b'=1}^{b-1} v_{bb'}, \quad h_b = K_b - Z/r_b,$$
$$v_{bb'} = 1/\max(r_b, r_{b'}), \quad K_b = -\frac{1}{2} d^2/dr_b^2, \tag{1}$$

where the subscript and superscript labeling of electrons is sometimes omitted hereafter to simplify notation, and atomic units are used throughout this manuscript.

The JM formalism [1,3] relies on the JM functions $\{\xi_p(r)\}_{p=0}^{\infty}$, such that $\xi_p(r=0)=0$ and $(K-E)$'s matrix is tridiagonal,

$$J_{pp'} = \langle \xi_p | K - E | \xi_{p'} \rangle,$$
$$J_{pp'} = 0, \quad \langle \xi_p | \xi_{p'} \rangle = 0, \quad |p - p'| > 1. \tag{2}$$

It is convenient to define an additional one-electron radial basis of N_t orthonormal functions $\{P_\lambda(r)\}_{\lambda=1}^{N_t}$ to describe the target electrons. Such a *target* basis is created from linear combinations of the first N_t JM functions

$$P_\lambda(r) = \sum_{p=0}^{N_t-1} D_{\lambda p}\xi_p(r), \quad \langle P_\lambda | P_{\lambda'} \rangle = \delta_{\lambda\lambda'}. \tag{3}$$

Under the considered frozen-core model of helium, one electron is frozen to be the *core* electron in the ground state

of the helium ion, which could be naturally obtained by diagonalizing the one-electron Hamiltonian h:

$$\langle P_\lambda|h|P_{\lambda'}\rangle = \varepsilon_\lambda \delta_{\lambda\lambda'}. \tag{4}$$

Note that λ's values start from one, while the JM function's index p starts from zero.

Following Fano [25], in the context of many electrons, each radial P_λ function could be used as the radial component of a *subshell*'s wave function. The subshell may contain a_λ *equivalent* electrons spin coupled into a state with the total spin s_λ and its z component μ_λ, and described by antisymmetrized wave function denoted by

$$|\psi_\lambda\rangle \equiv |(\lambda)^{a_\lambda} s_\lambda \mu_\lambda\rangle, \quad 1 \leqslant \lambda \leqslant N_t. \tag{5}$$

Since only $l = 0$ orbitals are considered, then $a_\lambda \in \{0,1,2\}$ and $s_\lambda \in \{0, \frac{1}{2}, 1\}$. Note that empty subshells are permitted ($a_\lambda = 0$, $s_\lambda = 0$) as they somewhat simplify notation and bookkeeping as per Cowan [26].

For a general case of a electrons and n available subshells, a particular electron configuration is labeled by index β and specified by an *unsymmetrized* wave function

$$|\phi_\beta\rangle \equiv |\mathbf{a}_\beta \mathbf{s}_\beta \mathbf{S}_\beta \mu_\beta\rangle, \tag{6}$$

where the vectors $\mathbf{a}_\beta$ and $\mathbf{s}_\beta$ describe electrons in n subshells via

$$\begin{aligned} \mathbf{a}_\beta &= (a_{\beta 1}, a_{\beta 2}, \ldots, a_{\beta n}), \quad \sum_{\lambda=1}^{n} a_{\beta\lambda} = a, \\ \mathbf{s}_\beta &= (s_{\beta 1}, s_{\beta 2}, \ldots, s_{\beta n}). \end{aligned} \tag{7}$$

Vector $\mathbf{S}_\beta$ denotes a coupling procedure by which the subshell spins $\mathbf{s}_\beta$ are consecutively coupled into the final total spin S_β and its z component μ_β. After omitting β labeling for brevity, the **S**-coupling procedure is expressed via

$$\mathbf{S} = (S_1 \equiv s_1, S_2, \ldots, S_n \equiv S), \tag{8}$$

$$|S_{\lambda-1} s_\lambda S_\lambda \mu\rangle = \sum_{\mu',\mu_\lambda} C^{S_\lambda \mu}_{S_{\lambda-1}\mu' s_\lambda \mu_\lambda} |S_{\lambda-1}\mu'\rangle\, |s_\lambda \mu_\lambda\rangle, \tag{9}$$

where $C^{jm}_{j_1 m_1 j_2 m_2} \equiv \langle j_1 m_1 j_2 m_2 | jm\rangle$ are the Clebsch-Gordan coefficients. To reiterate, $|\phi_\beta\rangle$ is antisymmetric in regard to the electrons from the same subshell and has all subshell spins consecutively coupled into the total spin S. The $|\phi_\beta\rangle$ states could be made fully antisymmetric via the antisymmetrization operator $\hat{A}$, denoting the result by $|\hat{A}\phi_\beta\rangle$.

B. JM method

This section uses the JM interpretation of Konovalov and Bray [7], which is here generalized to many-electron targets. For the specific case of the scattering problem, let a denote the number of electrons in the target. Then the a-electron square-integrable (L^2) target wave functions $\{\psi_\gamma\}$ are obtained by diagonalizing H_a [Eq. (1)] using Fano's subshell-structured electron configurations $\{\phi_\beta\}$ from the preceding section:

$$\begin{aligned} \langle\psi_\gamma|H_t|\psi_{\gamma'}\rangle &= e_\gamma \delta_{\gamma\gamma'}, \quad \langle\psi_\gamma|\psi_{\gamma'}\rangle = \delta_{\gamma\gamma'}, \\ |\psi_\gamma\rangle &= \sum_\beta C^t_{\gamma\beta} |\hat{A}\phi_\beta\rangle, \end{aligned} \tag{10}$$

where $H_t \equiv H_a$, $C^t_{\gamma\beta}$ are commonly referred to as the configuration-interaction (CI) coefficients, and where the set of $\{\phi_\beta\}$ [Eq. (6)] is labeled by index β in some arbitrary but fixed order.

The scattering problem is described by

$$(H - E)|\Psi_E\rangle = 0,$$

where $H \equiv H_{a+1}$ and E is the given total energy of the $(a+1)$-electron system. If the target is assumed to be in the γ_0 state before the collision, then

$$E = e_{\gamma_0} + E_0, \quad E_0 = k_0^2/2,$$

where E_0 is the incident electron energy.

Following Broad and Reinhardt [3] as much as relevant, the $\{\chi^\Gamma_\gamma\}$ channels are defined by spin coupling the target eigenstates $|\psi_\gamma\rangle$ and the spin of the scattering electron $s \equiv \frac{1}{2}$:

$$\begin{aligned} \left|\chi^\Gamma_\gamma\right\rangle &= \sum_{\mu\mu'} C^{S_\Gamma \mu_\Gamma}_{S_\gamma \mu' s\mu} |\psi_{\gamma\mu'}\rangle\, |s\mu\rangle, \\ \left|\phi^\Gamma_\beta\right\rangle &= \sum_{\mu\mu'} C^{S_\Gamma \mu_\Gamma}_{S_\beta \mu' s\mu} |\phi_{\beta\mu'}\rangle\, |s\mu\rangle, \end{aligned} \tag{11}$$

where $|s\mu\rangle$ is Pauli spinor, and where the corresponding basis channels $\{\phi^\Gamma_\beta\}$ are defined to be used later on [see Eq. (52)]. For the considered S-wave model, each scattering channel is labeled by a $\{\gamma,\Gamma\}$ pair, where $\Gamma = \{S_\Gamma, \mu_\Gamma\}$.

Within the JM method, the complete (and infinitely large) set of JM functions $\{\xi_p(r)\}_{p=0}^\infty$ is split into two subsets, defining the *outer* $(a+1)$-electron JM functions as

$$\begin{aligned} \left|\Phi^\Gamma_{\gamma p}\right\rangle &= \left|\chi^\Gamma_\gamma\right\rangle |\xi_p\rangle, \\ \left|\Psi^\Gamma_{\gamma p}\right\rangle &= \hat{A}^a_{a+1} \left|\Phi^\Gamma_{\gamma p}\right\rangle, \\ p &= N, N+1, \ldots, \infty \end{aligned} \tag{12}$$

where N is a key parameter of the JM method controlling the number of first JM functions omitted from the outer space, $\hat{A}^a_{a+1}$ denotes antisymmetrization of the $(a+1)$th electron in relation to already fully antisymmetrized a electrons, and where the explicit expression for $\hat{A}^a_{a+1}$ is given later [see Eq. (45)]. The antisymmetrization $\hat{A}^a_{a+1}$ could be accomplished in a practical fashion only if the target basis $\{P_\lambda(r)\}_{\lambda=1}^{N_t}$ defining the subshells in $\{\phi_\beta\}$ [Eq. (6)] is orthogonal to all *outer* JM functions $\{\xi_p(r)\}_{p=N}^\infty$. This forces [7]

$$N_t < N \tag{13}$$

when using tridiagonal JM functions such as the original nonorthogonal Laguerre basis [1,3]. Note that an orthogonal JM basis [27] is not considered hereafter, but modifications of the presented formalism to accommodate such a basis are expected to be straightforward.

To reproduce the original JM formulation [3], the *inner* $(a+1)$-electron basis should be constructed as

$$\begin{aligned} \left|\Phi^\Gamma_{\gamma\lambda}\right\rangle &= \left|\chi^\Gamma_\gamma\right\rangle |P_\lambda\rangle, \\ \left|\Psi^\Gamma_{\gamma\lambda}\right\rangle &= \hat{A}^a_{a+1} \left|\Phi^\Gamma_{\gamma\lambda}\right\rangle, \\ \lambda &= 1, 2, \ldots, N \end{aligned} \tag{14}$$

where the initial target basis $\{P_\lambda(r)\}_{\lambda=1}^{N_t}$ [Eq. (3)] is expanded by adding $(N-N_t)$ *transitional* basis functions created as linear combinations of the first N JM functions such that

$$\begin{aligned} P_\lambda(r) &= \sum_{p=0}^{N-1} D_{\lambda p}\xi_p(r), \quad N_t < \lambda \leqslant N \\ \langle P_\lambda | P_{\lambda'}\rangle &= \delta_{\lambda\lambda'}, \quad \lambda,\lambda' = 1,2,\ldots,N. \end{aligned} \tag{15}$$

The derivation of the final JM equations as well as some of the equations could be simplified if the $(a+1)$-electron eigenvectors of H are used instead of $\{\Psi^\Gamma_{\gamma\lambda}\}$ as the inner $(a+1)$-electron basis [7]. For a given Γ, such eigenvectors are obtained by diagonalizing H using all available distinct $(a+1)$-electron configurations $\{\Psi^\Gamma_{\gamma\lambda}\}$:

$$\begin{aligned} \left\langle \Psi^\Gamma_i \middle| H \middle| \Psi^\Gamma_j \right\rangle &= E_i\delta_{ij}, \quad \left\langle \Psi^\Gamma_i \middle| \Psi^\Gamma_j \right\rangle = \delta_{ij}, \\ \left|\Psi^\Gamma_j\right\rangle &= \sum_\gamma \sum_{\lambda=1}^{N} C^\Gamma_{j\gamma\lambda} \left|\Psi^\Gamma_{\gamma\lambda}\right\rangle. \end{aligned} \tag{16}$$

Having constructed eigenstate basis $\{\Psi^\Gamma_j\}$ functionally equivalent to $\{\Psi^\Gamma_{\gamma\lambda}\}$ [Eq. (14)], the full scattering wave function $|\Psi_E\rangle$ is approximated by the JM multichannel expansion [3,7]

$$\begin{aligned} |\Psi_E\rangle &\approx \sum_\Gamma \left|\Psi^\Gamma_N\right\rangle, \\ \left|\Psi^\Gamma_N\right\rangle &= \sum_j \left|\Psi^\Gamma_j\right\rangle a_j + \sum_\gamma \sum_{p=N}^{\infty} \left|\Psi^\Gamma_{\gamma p}\right\rangle f^{\gamma\gamma_0}_p, \\ f^{\gamma\gamma_0}_p &= (\pi|k_\gamma|/2)^{-1/2}\left(s^\gamma_p\delta_{\gamma\gamma_0} + c^\gamma_p R_{\gamma\gamma_0}\right), \end{aligned} \tag{17}$$

where $k_\gamma = \sqrt{2(E-e_\gamma)}$, and $R_{\gamma\gamma_0}$ is the unknown reactance matrix. Note that since the total spin S_Γ and its z projection μ_Γ are preserved in the considered scattering model, the $\Gamma \equiv \{S_\Gamma,\mu_\Gamma\}$ labeling will be mostly omitted but implied by the context. For example, all components in the last line of Eq. (17) are defined for a specific value of Γ.

The *open* channels are defined by $(E-e_\gamma) > 0$, while for the *closed* channels, $(E-e_\gamma) \leqslant 0$, $s^\gamma_p = 0$, and c^α_p is replaced by $(c^\gamma_p + \mathrm{i}s^\gamma_p)$ evaluated at $\mathrm{i}|k_\gamma|$. The index of the incident channel γ_0 is defined only for the open channels in Eq. (17). The a_j and $R_{\gamma\gamma_0}$ coefficients are found by simultaneously solving the following equations for the inner and outer functional spaces, respectively:

$$\begin{aligned} \left\langle \Psi^\Gamma_i \middle| H - E \middle| \Psi^\Gamma_N \right\rangle &= 0, \\ \left\langle \Psi^\Gamma_{\gamma' p'} \middle| H - E \middle| \Psi^\Gamma_N \right\rangle &= 0, \quad p' \geqslant N. \end{aligned} \tag{18}$$

The two key JM multichannel approximations [3], denoted by JM1 and JM2, could be summarized as

$$\mathrm{JM1}: \left\langle \Psi^\Gamma_{\gamma' p'} \middle| H - E \middle| \Psi^\Gamma_{\gamma p} \right\rangle \approx \delta_{\gamma\gamma'} J^\gamma_{p'p}, \tag{19}$$

$$\mathrm{JM2}: \left\langle \Psi^\Gamma_i \middle| H - E \middle| \Psi^\Gamma_{\gamma p} \right\rangle \approx \delta_{pN} J^\gamma_{N-1,N} X^\gamma_i, \tag{20}$$

where Eq. (20) defines X^γ_i, and where

$$J^\gamma_{p'p} = \langle \xi_{p'} | K - (E-e_\gamma) | \xi_p \rangle. \tag{21}$$

Using the JM1 and JM2 approximations, Eq. (18) is reduced to

$$\begin{aligned} (E_i - E)a_i &= -\sum_\gamma X^\gamma_i J^\gamma_{N-1,N} f^{\gamma\gamma_0}_N, \\ \sum_j X^{\gamma'}_j a_j &= f^{\gamma'\gamma_0}_{N-1}, \end{aligned}$$

and after elimination of a_i to

$$\begin{aligned} \sum_\gamma W_{\gamma'\gamma} J^\gamma_{N-1,N} f^{\gamma\gamma_0}_N &= -f^{\gamma'\gamma_0}_{N-1}, \\ W_{\gamma'\gamma} &= \sum_j X^{\gamma'}_j X^\gamma_j / (E_j - E). \end{aligned} \tag{22}$$

Solving Eq. (22) for the reactance matrix yields

$$\begin{aligned} R_{\gamma\gamma_0} &= -\sum_{\gamma'} Z^{-1}_{\gamma\gamma'} Y_{\gamma'\gamma_0}, \\ Y_{\gamma'\gamma} &= \left(W_{\gamma'\gamma} J^\gamma_{N-1,N} s^\gamma_N + \delta_{\gamma\gamma'} s^\gamma_{N-1}\right)/\sqrt{|k_\gamma|}, \\ Z_{\gamma'\gamma} &= \left(W_{\gamma'\gamma} J^\gamma_{N-1,N} c^\gamma_N + \delta_{\gamma\gamma'} c^\gamma_{N-1}\right)/\sqrt{|k_\gamma|}. \end{aligned}$$

Using only the open-channel portion of R, the scattering matrix $\hat{S}$ and cross sections are given by [3]

$$\begin{aligned} \hat{S}^\Gamma_{\gamma\gamma_0} &= \sum_{\gamma':e_{\gamma'}\leqslant E} (1+\mathrm{i}R)_{\gamma\gamma'}(1-\mathrm{i}R)^{-1}_{\gamma'\gamma_0}, \\ \sigma^\Gamma_{\gamma\gamma_0} &= \pi k^{-2}_{\gamma_0} \left|\hat{S}^\Gamma_{\gamma\gamma_0} - \delta_{\gamma\gamma_0}\right|^2, \\ \sigma_{\gamma\gamma_0} &= [2(2S_{\gamma_0}+1)]^{-1} \sum_{S_\Gamma} (2S_\Gamma+1)\sigma^\Gamma_{\gamma\gamma_0}, \end{aligned}$$

where only the open scattering channels ($e_{\gamma'} \leqslant E$) are used in $\sum_{\gamma'}$, and where $\sigma_{\gamma\gamma_0}$ is the cross section for the transition from γ_0 to γ states of the target.

In the case of the considered frozen-core model, the total *single*-ionization cross section (TSICS) is naturally defined as

$$\sigma_\mathrm{I} \equiv \sigma_\mathrm{TSICS} \approx \sum_{\gamma:e_\gamma > \varepsilon_{1s}} \sigma_{\gamma\gamma_0}, \tag{23}$$

where ψ_{γ_0} is the state of the target helium atom with the lowest eigenvalue from Eq. (10), and where $\varepsilon_{1s} \equiv \varepsilon[\mathrm{He}^+(1s)]$ is the lowest eigenvalue from Eq. (4). Since one of the target electrons is always in the $\mathrm{He}^+(1s)$ state, any two-electron target state ψ_γ [Eq. (10)] with its energy $e_\gamma > \varepsilon_{1s}$ is interpreted as an L^2-continuum state contributing to TSICS [7].

C. Many-electron matrix elements

This section summarizes the general equations of Fano [25], Shore [28], and Cowan [26] for multiconfiguration matrix elements. Let q_b denote the radial r_b and spin ν_b coordinates of the bth electron and $\mathbf{q}$ denote the naturally ordered arrangement of a-electron coordinates

$$\mathbf{q} \equiv (q_1,q_2,\ldots,q_a), \quad q_b \equiv (r_b,\nu_b). \tag{24}$$

Let n denote the number of available subshells, then the first a_1 coordinates are assigned to the first subshell [Eq. (5)], the next a_2 coordinates to the second, and so on:

$$\begin{aligned}\Phi(\mathbf{q}) \equiv \langle \mathbf{q}|\Phi\rangle = \sum &\text{ spin coupling as per } \mathbf{S}\\ &\times \left\langle q_1, q_2, \ldots, q_{a_1}\middle|(1)^{a_1} s_1 \mu_1\right\rangle\\ &\times \left\langle q_{a_1+1}, q_{a_1+2}, \ldots, q_{a_1+a_2}\middle|(2)^{a_2} s_2 \mu_2\right\rangle\\ &\ldots\\ &\times \left\langle q_{a-a_n+1}, q_{a-a_n+2}, \ldots, q_a\middle|(n)^{a_n} s_n \mu_n\right\rangle.\end{aligned}$$

The antisymmetrization equation for $|\hat{A}\Phi\rangle$, corresponding to Fano's Eq. (8), becomes

$$\hat{A}\Phi(\mathbf{q}) = \mathcal{N}(\mathbf{a})^{-1/2} \sum_Q (-1)^{P_Q} \Phi(Q), \tag{25}$$

where Q denotes a particular rearrangement or permutation of the natural order $\mathbf{q}$, $\mathcal{N}(\mathbf{a})$ is the number of such distinct permutations, and a parity P_Q is the minimum number of pairwise permutations required to arrive at Q from $\mathbf{q}$. By its construction, $\Phi(\mathbf{q})$ is already antisymmetric in regard to the electrons from the same subshells; therefore, Q must be limited only to the cases when the electrons are swapped between different subshells rather than within the subshells. The corresponding combinatorics problem is the partitioning of a set containing a elements into subsets containing $a_1, a_2, \ldots, a_n$ elements, arriving at

$$\mathcal{N}(\mathbf{a}) = a! \Big/ \prod_{\lambda=1}^{n} a_\lambda !.$$

Given fully antisymmetric a-electron basis $\hat{A}\Phi(\mathbf{q})$, each element of the one- and two-electron summation terms in Eq. (1) contributes equally arriving at

$$\begin{aligned}\langle \hat{A}\Phi|H_a|\hat{A}\Phi'\rangle &= \langle h\rangle + \langle v\rangle,\\ \langle h\rangle &= a\langle \hat{A}\Phi|h_a|\hat{A}\Phi'\rangle,\\ \langle v\rangle &= a(a-1)\langle \hat{A}\Phi|v_{a,a-1}|\hat{A}\Phi'\rangle/2,\end{aligned} \tag{26}$$

where only the last electron coordinate q_a (in both $\langle h\rangle$ and $\langle v\rangle$) and electron coordinate q_{a-1} (in $\langle v\rangle$) are left as the *interacting* electrons, and where the remaining (first $a-1$ or $a-2$) electrons are referred to as the *spectator* electrons [25].

Focusing on $\langle v\rangle$ and using Eqs. (25) and (26), $\langle v\rangle$ becomes

$$\begin{aligned}\langle v\rangle = &\tfrac{1}{2} a(a-1)[\mathcal{N}(\mathbf{a})\mathcal{N}(\mathbf{a}')]^{-1/2}\\ &\times \sum_{Q,Q'} (-1)^{P_Q + P_{Q'}} \langle \Phi(Q)|v|\Phi'(Q')\rangle,\end{aligned}$$

which is equivalent of Fano's Eq. (12), and where $v \equiv v_{a,a-1}$. By the orthogonality of one-electron radial wave functions of different subshells, the distribution of the spectator electrons

$$\bar{\mathbf{a}} = (\bar{a}_1, \bar{a}_2, \ldots, \bar{a}_n), \quad \sum_{\lambda=1}^{n} \bar{a}_\lambda = a-2, \tag{27}$$

must be identical on both sides of $\langle v\rangle$ obtaining potentially nonzero contributions only when $\bar{\mathbf{a}} \equiv \bar{\mathbf{a}}'$. By explicitly specifying subshell location of the interacting electrons, the following parametrization becomes possible:

$$\begin{aligned}\bar{a}_\lambda &= a_\lambda - \delta_{\lambda\rho} - \delta_{\lambda\sigma}, \quad \rho \leqslant \sigma\\ \bar{a}'_\lambda &= a'_\lambda - \delta_{\lambda\rho'} - \delta_{\lambda\sigma'}, \quad \rho' \leqslant \sigma'\end{aligned} \tag{28}$$

where (ρ,σ) and (ρ',σ') are the subshells of the two interacting electrons from the respective sides of $\langle v\rangle$. Then, for each *valid* (potentially nonzero matrix element) distribution of the interacting electrons, there are

$$\mathcal{N}(\bar{\mathbf{a}}') \equiv \mathcal{N}(\bar{\mathbf{a}}) = (a-2)! \Big/ \prod_{\lambda=1}^{n} (a_\lambda - \delta_{\lambda\rho} - \delta_{\lambda\sigma})!$$

valid and equally contributing distributions of the spectator electrons arriving at [Fano's Eqs. (18) and (22)]

$$\begin{aligned}\sum_{Q,Q'} \to &\sum_{\rho\leqslant\sigma,\rho'\leqslant\sigma'} [\mathcal{N}(\bar{\mathbf{a}})\mathcal{N}(\bar{\mathbf{a}}')]^{1/2}\\ &\times \sum_{\epsilon,\epsilon'=0,1} (1-\epsilon\delta_{\rho\sigma})(1-\epsilon'\delta_{\rho'\sigma'}),\\ \langle v\rangle = &\frac{1}{2} \sum_{\rho\leqslant\sigma,\rho'\leqslant\sigma'} \mathcal{N}_{\rho\sigma}(\mathbf{a})\mathcal{N}_{\rho'\sigma'}(\mathbf{a}')\\ &\times \sum_{\epsilon,\epsilon'=0,1} A(Q)A(Q')\langle \Phi(Q)|v|\Phi'(Q')\rangle,\\ \mathcal{N}_{\rho\sigma}(\mathbf{a}) = &[a_\rho(a_\sigma - \delta_{\rho\sigma})]^{1/2},\\ A(Q) = &(1-\epsilon\delta_{\rho\sigma})(-1)^{P_Q},\end{aligned} \tag{29}$$

where $\mathcal{N}_{\rho'\sigma'}(\mathbf{a}')$ and $A(Q')$ are defined in identical fashion to the corresponding nonprimed entities, and where $\epsilon = 0$ is the natural order denoting $q_{a-1} \in \rho$, $q_a \in \sigma$, and $\epsilon = 1$ denotes the swapped order, i.e., $q_a \in \rho$, $q_{a-1} \in \sigma$.

As per Cowan [26], the difference in parity between Q and Q' is given by (modulo 2)

$$\begin{aligned}P_Q + P_{Q'} &= \Delta P + \epsilon - \epsilon',\\ \Delta P &= \Delta P_Q - \Delta P_{Q'},\\ \Delta P_Q &= \delta_{\rho\sigma} - 1 + \sum_{\lambda=\rho+1}^{\sigma} a_\lambda,\end{aligned} \tag{30}$$

where $\Delta P_{Q'}$ is defined in identical fashion to ΔP_Q. For $\epsilon = 0$, the preceding equations are derived by observing that it requires

$$P_\sigma = \sum_{\lambda=\sigma+1}^{n} a_\lambda \tag{31}$$

coordinate interchanges to move q_a from the σth subshell (where q_a ended up due to Q) and into the last nonempty subshell as the last coordinate. Similarly, it requires

$$P_\rho = \delta_{\rho\sigma} - 1 + \sum_{\lambda=\rho+1}^{n} a_\lambda$$

coordinate interchanges for q_{a-1} to be moved into the highest possible subshell *after* the ordering of q_a, obtaining (again modulo 2)

$$P_Q = P_{\bar{Q}} + \Delta P_Q, \quad \Delta P_Q = P_\sigma - P_\rho + \epsilon,$$

where $P_{\bar{Q}}$ is the parity due to the spectator electrons, which is identical to $P_{\bar{Q}'}$ and therefore disappears from Eq. (30). Note

that Fano [25] derived a different form of ΔP_Q in Eq. (30), i.e.,

$$\Delta P_Q^{\text{Fano}} = \sum_{\lambda=\rho+1}^{\sigma} \bar{a}_\lambda,$$

which could be reduced to the preceding Cowan's form via Eq. (28).

And, finally, by using Eq. (30) and explicitly showing the *direct* and *exchange* terms, Eq. (29) is reduced to the arguably more compact Cowan's form [26]

$$\begin{aligned}\langle v\rangle &= \sum_{\rho\leqslant\sigma,\rho'\leqslant\sigma'} \mathcal{N}_{\rho\sigma}(\mathbf{a})\mathcal{N}_{\rho'\sigma'}(\mathbf{a}')(-1)^{\Delta P} \\ &\quad\times [v_{\text{di}} - (1-\delta_{\rho\sigma})(1-\delta_{\rho'\sigma'})v_{\text{ex}}]/(1+\delta_{\rho\sigma}\delta_{\rho'\sigma'}), \quad (32)\\ v_{\text{di}} &\equiv \langle\Phi_{\rho\sigma}|v|\Phi'_{\rho'\sigma'}\rangle, \quad v_{\text{ex}} \equiv \langle\Phi_{\rho\sigma}|v|\Phi'_{\sigma'\rho'}\rangle,\end{aligned}$$

where v_{di} and v_{ex} denote the direct and exchange contributions, respectively, and where

$$\Phi_{\rho\sigma}(\mathbf{q}) \equiv \Phi(q_{a-1}\in\rho, q_a\in\sigma) \quad (33)$$

denotes a permutation of $\mathbf{q}$ when q_{a-1} and q_a are moved to the ρth and σth subshells, respectively.

Repeating the preceding steps for $\langle h\rangle$, Eq. (26) is reduced to

$$\langle h\rangle = \sum_{\sigma,\sigma'}[a_\sigma a_{\sigma'}]^{1/2}(-1)^{P_\sigma+P_{\sigma'}}\langle\Phi_\sigma|h_a|\Phi'_{\sigma'}\rangle, \quad (34)$$

where P_σ is defined by Eq. (31), and where $\Phi_\sigma(\mathbf{q}) \equiv \Phi(q_a\in\sigma)$ denotes a permutation of $\mathbf{q}$ when q_a is moved to the σth subshell. If (and only if) the radial component of the subshell wave functions on both sides are built exclusively from the eigenvectors of h as per Eq. (4), then Eq. (34) could be further reduced to the following well-known form:

$$\langle h\rangle = \langle\Phi|\Phi'\rangle\sum_\lambda a_\lambda\varepsilon_\lambda.$$

D. Electron-helium scattering matrix elements

The goal here is to express all required matrix elements in terms of Fano's matrix elements [25] from the preceding section, which are defined for any antisymmetric many-electron wave functions expressed in terms of subshells.

For the specific case of the S-wave model of scattering, the radial integration in Eq. (32) yields

$$\begin{aligned}\langle\Phi_{\rho\sigma}|v|\Phi'_{\rho'\sigma'}\rangle &= \delta_{SS'}\delta_{\mu\mu'}\delta_{\bar{\mathbf{a}}\bar{\mathbf{a}}'}R^0_{\rho\sigma\rho'\sigma'}S(\rho\sigma,\rho'\sigma'),\\ R^0_{\rho\sigma\rho'\sigma'} &= \int_0^\infty\int_0^\infty dr_1dr_2\frac{P_\rho(r_1)P_\sigma(r_2)P_{\rho'}(r_1)P_{\sigma'}(r_2)}{\max(r_1,r_2)},\\ S(\rho\sigma,\rho'\sigma') &= \langle\Phi_{\rho\sigma}|\Phi'_{\rho'\sigma'}\rangle, \quad (35)\end{aligned}$$

where only spin variables are considered in $S(\rho\sigma,\rho'\sigma')$. Since $\delta_{SS'}\delta_{\mu\mu'}$ are accounted for in Eq. (35), both $\Phi_{\rho\sigma}$ and $\Phi'_{\rho'\sigma'}$ will be assumed to have the same total spin S and its z component μ.

The case of helium target wave functions with just two electrons becomes

$$S(\rho\sigma,\rho'\sigma') = (-1)^{\epsilon(1-S)}, \quad (36)$$

where ϵ is reused to indicate the direct ($\epsilon=0$) and exchange ($\epsilon=1$) terms from Eq. (32).

For three-electron wave functions with a single fixed spectator electron, the **S**-coupling procedure from Eqs. (8) and (9) yields the following exhaustive set of spin-coupling schemas:

$$\begin{aligned}|A_1\rangle &\equiv |\lambda\rho(S_\rho)\sigma\rangle, \quad \lambda\leqslant\rho<\sigma\\ |A_2\rangle &\equiv |\rho\lambda(S_\lambda)\sigma\rangle, \quad \rho<\lambda<\sigma\\ |B_1\rangle &\equiv |\rho\sigma(S_\sigma)\lambda\rangle, \quad \rho\leqslant\sigma<\lambda\\ |B_2\rangle &\equiv |\lambda,\rho\sigma(s_\rho\equiv 0)\rangle, \quad \lambda<\rho, \quad \rho=\sigma\\ |B_3\rangle &\equiv |\rho,\lambda\sigma(s_\sigma\equiv 0)\rangle, \quad \rho<\sigma, \quad \lambda=\sigma\end{aligned}$$

where (i) the first two and the last three schemas are grouped together and denoted schemas A and B, respectively; (ii) the subshell indexes are explicitly shown, while the actual electron spin value $s=\frac{1}{2}$ is suppressed; and (iii) the intermediate spins are displayed in brackets. For example, $\lambda\rho(S_\rho)$ denotes coupling into S_ρ of spins of electrons from λth and ρth subshells. If, by construction, all possible left-to-right cases of coupling are considered as per Eqs. (8) and (9), then such a right-to-left case as $|\lambda,\rho\sigma(S_\sigma)\rangle$, $\lambda<\rho<\sigma$, never occurs. Moreover, any omitted right-to-left coupling schemas are redundant (linear dependent) since they could be constructed as linear combinations of the left-to-right cases via the standard $6j$ recoupling expressions

$$\begin{aligned}&\langle j_1j_2(j_{12}),j_3:J|j_1,j_2j_3(j_{23}):J\rangle\\ &\quad= (-1)^{j_1+j_2+j_3+J}\hat{j}_{12}\hat{j}_{23}\begin{Bmatrix} j_1 & j_2 & j_{12}\\ j_3 & J & j_{23}\end{Bmatrix}, \quad (37)\end{aligned}$$

where $\hat{j}=\sqrt{2j+1}$, and where, for example,

$$\begin{Bmatrix} s & s & S_{12}\\ s & s & 0\end{Bmatrix} = \begin{Bmatrix} s & s & 0\\ s & s & S_{12}\end{Bmatrix} = \frac{1}{2}(-1)^{1+S_{12}}. \quad (38)$$

Naturally, the chosen left-to-right procedure does not have any advantages over the right-to-left procedure (or any other spin-coupling procedure) providing all available linear independent schemas are considered.

To clarify the notation and to assist with the exchange terms, the following example explicitly shows all spin variables:

$$\begin{aligned}\langle\nu_3\nu_1\nu_2|\lambda\rho(S_\rho)\sigma\rangle &= \sum_{\mu_3\mu_1\mu_\rho} C^{S_\rho\mu_\rho}_{s\mu_3s\mu_1}C^{S\mu}_{S_\rho\mu_\rho s\mu_2}\\ &\quad\times\langle\nu_3|s\mu_3\rangle\langle\nu_1|s\mu_1\rangle\langle\nu_2|s\mu_2\rangle\\ &= C^{S_\rho\mu_\rho}_{s\nu_3s\nu_1}C^{S\mu}_{S_\rho\mu_\rho s\nu_2}, \quad (39)\end{aligned}$$

where $\langle\nu|s\mu\rangle=\delta_{\nu\mu}$ are the components of Pauli spinor, and where ν_3, ν_1, and ν_2 are the spin coordinates of the spectator, ρth, and σth electrons, respectively. Note that if the spectator and interacting electrons belong to the same subshell ($\lambda=\rho$), then $S_\lambda=S_\rho=0$.

Unfortunately, the chosen Fano's formalism yields relatively compact close-form expressions only up to this point, after which the remaining matrix elements must be tabulated. Considering the corresponding primed schemas and using properties of the Clebsch-Gordan coefficients such as

$$|j_1j_2(j)\rangle = (-1)^{j_1+j_2-j}|j_2j_1(j)\rangle, \quad (40)$$

the total of four *direct* A-A' combinations are reduced to

$$\begin{aligned} \langle A_1|A'_1\rangle_{\rm di} &= \delta_{S_\rho S_{\rho'}}, \quad \langle A_1|A'_2\rangle_{\rm di} = \delta_{S_\rho S'_\lambda}(-1)^{1-S'_\lambda}, \\ \langle A_2|A'_2\rangle_{\rm di} &= \delta_{S_\lambda S'_\lambda}, \quad \langle A_2|A'_1\rangle_{\rm di} = \delta_{S_\lambda S_{\rho'}}(-1)^{1-S_\lambda}. \end{aligned} \tag{41}$$

The *exchange* terms are best explained by Eq. (39), where ν_1 and ν_2 must be swapped to obtain the exchange term from Eq. (32). For example, the following explicitly shows how the exchange term corresponding to the first combination in Eq. (41) could be evaluated using Eqs. (37), (39), and (40):

$$\begin{aligned} \langle A_1|A'_1\rangle_{\rm ex} &\equiv \langle \lambda\rho(S_\rho)\sigma|\lambda\sigma'(S_{\rho'})\rho'\rangle \\ &= \sum_{\nu_1\nu_2\nu_3} \langle \lambda\rho(S_\rho)\sigma|\nu_3\nu_1\nu_2\rangle\langle\nu_3\nu_2\nu_1|\lambda\rho'(S_{\rho'})\sigma'\rangle \\ &= \sum_{\nu_1\nu_2\nu_3\mu_\rho\mu_{\rho'}} C^{S_\rho\mu_\rho}_{s\nu_3 s\nu_1} C^{S\mu}_{S_\rho\mu_\rho s\nu_2} C^{S_{\rho'}\mu_{\rho'}}_{s\nu_3 s\nu_2} C^{S\mu}_{S_{\rho'}\mu_{\rho'} s\nu_1} \\ &= (-1)^{1-S_\rho+S_{\rho'}+s-S}\langle\rho\lambda(S_\rho)\sigma|\rho',\lambda\sigma'(S_{\rho'})\rangle \\ &= (-1)^{1-S_\rho+S_{\rho'}}\hat{S}_\rho\hat{S}_{\rho'}\begin{Bmatrix} s & s & S_\rho \\ s & S & S_{\rho'}\end{Bmatrix}. \end{aligned}$$

The remaining exchange A-A' combinations become

$$\begin{aligned} \langle A_1|A'_2\rangle_{\rm ex} &= (-1)^{S_\rho}\hat{S}_\rho\hat{S}'_\lambda\begin{Bmatrix} s & s & S_\rho \\ s & S & S'_\lambda\end{Bmatrix}, \\ \langle A_2|A'_2\rangle_{\rm ex} &= -\hat{S}_\lambda\hat{S}'_\lambda\begin{Bmatrix} s & s & S_\lambda \\ s & S & S'_\lambda\end{Bmatrix}, \end{aligned}$$

where hereafter the terms that are different only in primes are omitted, for example $\langle A_2|A'_1\rangle$ could be obtained from $\langle A_1|A'_2\rangle$ by swapping the primes. Using Eq. (38) and recalling that exchange terms are required only when both $\rho \neq \sigma$ and $\rho' \neq \sigma'$, the B-B' combinations are reduced to

$$\begin{aligned} \langle B_1|B'_1\rangle &= (-1)^{\epsilon(1-S_{\sigma'})}\delta_{S_\sigma S_{\sigma'}}, \\ \langle B_1|B'_2\rangle &= \delta_{sS}\delta_{0S_\sigma}, \\ \langle B_1|B'_3\rangle &= \tfrac{1}{2}(-1)^{\epsilon(1-S_\sigma)+S_\sigma}\delta_{sS}\hat{S}_\sigma, \\ \langle B_2|B'_2\rangle &= \delta_{sS}, \\ \langle B_2|B'_3\rangle &= \tfrac{1}{2}\delta_{sS}, \\ \langle B_3|B'_3\rangle_{\rm di} &= \delta_{sS}, \quad \langle B_3|B'_3\rangle_{\rm ex} = \tfrac{1}{2}\delta_{sS}, \end{aligned}$$

where the exchange terms are parameterized as per Eq. (36).

The following are all required A-B' combinations:

$$\begin{aligned} \langle A_1|B'_1\rangle &= (-1)^{\epsilon(1-S_{\sigma'})+S_{\sigma'}}\hat{S}_\rho\hat{S}_{\sigma'}\begin{Bmatrix} s & s & S_\rho \\ s & S & S_{\sigma'}\end{Bmatrix}, \\ \langle A_1|B'_2\rangle &= \tfrac{1}{2}\delta_{sS}(-1)^{1+S_\rho}\hat{S}_\rho, \\ \langle A_1|B'_3\rangle_{\rm di} &= \tfrac{1}{2}\delta_{sS}\hat{S}_\rho, \quad \langle A_1|B'_3\rangle_{\rm ex} = \delta_{sS}\delta_{0S_\rho}, \\ \langle A_2|B'_1\rangle &= (-1)^{\epsilon(1-S_{\sigma'})+1-S_\lambda+S_{\sigma'}}\hat{S}_\lambda\hat{S}_{\sigma'}\begin{Bmatrix} s & s & S_\lambda \\ s & S & S_{\sigma'}\end{Bmatrix}, \\ \langle A_2|B'_2\rangle &= \tfrac{1}{2}\delta_{sS}\hat{S}_\lambda, \\ \langle A_2|B'_3\rangle_{\rm di} &= \tfrac{1}{2}\delta_{sS}(-1)^{1+S_\lambda}\hat{S}_\lambda, \quad \langle A_2|B'_3\rangle_{\rm ex} = -\delta_{sS}\delta_{0S_\lambda}, \end{aligned}$$

where the B-A' terms could be obtained from the preceding equations by swapping the primes.

Repeating the preceding steps for the one-electron interactions, the radial integration in Eq. (34) yields

$$\begin{aligned} \langle\Phi_\rho|h|\Phi'_{\rho'}\rangle &= \delta_{SS'}\delta_{\mu\mu'}\delta_{\bar{\mathbf{a}}\bar{\mathbf{a}}'}h_{\rho\rho'}S(\rho,\rho'), \\ h_{\rho\rho'} &= \int_0^\infty dr\ P_\rho(r)hP_{\rho'}(r), \end{aligned} \tag{42}$$

$$S(\rho,\rho') = \langle\Phi_\rho|\Phi'_{\rho'}\rangle, \tag{43}$$

where again only spin variables are considered in Eq. (43). If $h_{\rho\rho'} = 0$ for $\rho \neq \rho'$, then it is not possible to select the same spectator electrons in both Φ_ρ and Φ'_ρ in any cross-schema matrix elements arriving at $S(\rho,\rho') = \delta_{\mathbf{SS}'}$ and, hence,

$$\langle\Phi_\rho|h|\Phi'_{\rho'}\rangle = \delta_{\mathbf{SS}'}\delta_{\mu\mu'}\delta_{\rho\rho'}h_{\rho\rho}.$$

Note that while it is interesting to examine the one-electron interactions in theory, in practice [6], it is simpler just to include the one-electron terms into v_{12} in Eq. (26):

$$\begin{aligned} \langle\hat{A}\Phi|H_a|\hat{A}\Phi'\rangle &= a(a-1)\langle\hat{A}\Phi|\hat{v}|\hat{A}\Phi'\rangle/2, \\ \hat{v} &= v_{a,a-1} + (h_{a-1}+h_a)/(a-1), \end{aligned}$$

and then combine Eqs. (35) and (42), i.e.,

$$\begin{aligned} \langle\Phi_{\rho\sigma}|\hat{v}|\Phi'_{\rho'\sigma'}\rangle &= \delta_{\mathbf{SS}'}\delta_{\mu\mu'}\delta_{\bar{\mathbf{a}}\bar{\mathbf{a}}'}\hat{R}^0_{\rho\sigma\rho'\sigma'}S(\rho\sigma,\rho'\sigma'), \\ \hat{R}^0_{\rho\sigma\rho'\sigma'} &= R^0_{\rho\sigma\rho'\sigma'} + \frac{1}{a-1}(h_{\rho\rho'}\delta_{\sigma\sigma'} + \delta_{\rho\rho'}h_{\sigma\sigma'}). \end{aligned}$$

E. JM approximations

In this section, the JM1 [Eq. (19)] and JM2 [Eq. (20)] approximations are examined in detail. Using the explicit forms of $|\chi^\Gamma_\gamma\rangle$ [Eq. (11)] and $|\Psi^\Gamma_{\gamma p}\rangle$ [Eq. (12)], the common part of JM1 and JM2 is approximated as

$$\begin{aligned} (H-E)\big|\Psi^\Gamma_{\gamma p}\big\rangle &= (H-E)\hat{A}^a_{a+1}\big|\Phi^\Gamma_{\gamma p}\big\rangle \\ &= (H-E)\hat{A}^a_{a+1}\big|\chi^\Gamma_\gamma\big\rangle|\xi_p\rangle \\ &= \hat{A}^a_{a+1}(H-E)\big|\chi^\Gamma_\gamma\big\rangle|\xi_p\rangle \\ &\approx \hat{A}^a_{a+1}\big|\chi^\Gamma_\gamma\big\rangle(K+e_\gamma-E)|\xi_p\rangle. \end{aligned} \tag{44}$$

The required antisymmetrization $\hat{A}^a_{a+1}|\Phi^\Gamma_{\gamma p}\rangle$ could be expressed in notation of Eqs. (24) and (25) as

$$\begin{aligned} \Psi^\Gamma_{\gamma p}(\mathbf{q},q_{a+1}) &= \hat{A}^a_{a+1}\Phi^\Gamma_{\gamma p}(\mathbf{q},q_{a+1}) \\ &= (a+1)^{-1/2}\sum_{b=1}^{a+1}(-1)^{P_{Q_b}}\Phi^\Gamma_{\gamma p}(Q_b,q_b), \\ \Phi^\Gamma_{\gamma p}(\mathbf{q},q_{a+1}) &\equiv \chi^\Gamma_\gamma(\mathbf{q},\nu_{a+1})\xi_p(r_{a+1}), \\ \Phi^\Gamma_{\gamma p}(Q_b,q_b) &\equiv \chi^\Gamma_\gamma(Q_b,\nu_b)\xi_p(r_b), \end{aligned} \tag{45}$$

where Q_b denotes replacement of q_b coordinate by q_{a+1} in $\mathbf{q} \equiv (q_1,q_2,\ldots,q_a)$, that is, $Q_{a+1} \equiv \mathbf{q}$ and

$$Q_b \equiv (q_1,q_2,\ldots,q_{b-1},q_{a+1},q_{b+1},\ldots,q_a).$$

The JM1 approximation is examined by substituting Eqs. (44) and (45) into Eq. (19), arriving at

$$\begin{aligned}&\langle\Psi^\Gamma_{\gamma'p'}|H-E|\Psi^\Gamma_{\gamma p}\rangle\\&\quad\approx\frac{1}{a+1}\sum_{b'b}(-1)^{P_{Q_{b'}}+P_{Q_b}}\\&\qquad\times\langle\Phi^\Gamma_{\gamma'p'}(Q_{b'},q_{b'})|(K_b+e_\gamma-E)|\Phi^\Gamma_{\gamma p}(Q_b,q_b)\rangle\\&\quad=\langle\chi^\Gamma_{\gamma'}|\chi^\Gamma_\gamma\rangle\langle\xi_{p'}|K+e_\gamma-E|\xi_p\rangle=\delta_{\gamma'\gamma}J^\gamma_{p'p},\end{aligned}\tag{46}$$

where the contributions from nondiagonal permutations $Q_{b'}$ and $Q_{b\neq b'}$ vanish. Hence, the effect of the two antisymmetrization operators is reduced to permutations with identical radial coordinate in both $\xi_{p'}(r_b)$ and $\xi_p(r_b)$. That is, for $b'\neq b$, $p\geqslant N$ and $p'\geqslant N$,

$$\begin{aligned}&\langle\Phi^\Gamma_{\gamma'p'}(Q_{b'},q_{b'})|(K_b+e_\gamma-E)|\Phi^\Gamma_{\gamma p}(Q_b,q_b)\rangle\\&\quad\sim\langle\psi_{\gamma'}(Q_{b'})\xi_{p'}(r_{b'})|\psi_\gamma(Q_b)(K_b+e_\gamma-E)\xi_p(r_b)\rangle\\&\quad\sim\sum_{\lambda'=1}^{N_t}\sum_{\lambda=1}^{N_t}c_{\gamma'\lambda'}c_{\gamma\lambda}\\&\qquad\times\langle\xi_{p'}|P_\lambda\rangle\,\langle P_{\lambda'}|(K+e_\gamma-E)|\xi_p\rangle=0,\end{aligned}$$

where $c_{\gamma\lambda}$ are some expansion coefficients in the most general sense, and where every potentially contributing term in the last double summation is exactly zero. In this particular case, both contributing factors are zeros:

$$\langle\xi_p|P_\lambda\rangle=0,\quad\langle P_\lambda|(K+e_\gamma-E)|\xi_p\rangle=0,\qquad p\geqslant N,\quad 1\leqslant\lambda\leqslant N_t$$

due to the target basis $\{P_\lambda\}_{\lambda=1}^{N_t}$ being orthogonal to the outer JM functions $\{\xi_p\}_{p=N}^\infty$ [see explanation for Eq. (13)].

For the JM2 [Eq. (20)] approximation and in steps similar to Eq. (46), Ψ^Γ_i could be explicitly written using Eq. (16) arriving at

$$\begin{aligned}&\langle\Psi^\Gamma_i|H-E|\Psi^\Gamma_{\gamma p}\rangle\\&\quad\approx\sum_{\gamma'}\sum_{\lambda=1}^{N}C^\Gamma_{i\gamma'\lambda}\frac{1}{a+1}\sum_{b'b}(-1)^{P_{Q_{b'}}+P_{Q_b}}\\&\qquad\times\langle\Phi^\Gamma_{\gamma'\lambda}(Q_{b'},q_{b'})|(K_b+e_\gamma-E)|\Phi^\Gamma_{\gamma p}(Q_b,q_b)\rangle\\&\quad=\sum_{\lambda=1}^{N}C^\Gamma_{i\gamma\lambda}\langle P_\lambda|K+e_\gamma-E|\xi_p\rangle.\end{aligned}\tag{47}$$

The corresponding expression for nondiagonal permutations becomes

$$\begin{aligned}&\langle\Phi^\Gamma_{\gamma'\lambda}(Q_{b'},q_{b'})|(K_b+e_\gamma-E)|\Phi^\Gamma_{\gamma p}(Q_b,q_b)\rangle\\&\quad\sim\langle\psi_{\gamma'}(Q_{b'})P_\lambda(r_{b'})|\psi_\gamma(Q_b)(K_b+e_\gamma-E)\xi_p(r_b)\rangle\\&\quad\sim\sum_{\lambda'=1}^{N_t}\sum_{\lambda''=1}^{N_t}c_{\gamma'\lambda'}c_{\gamma\lambda''}\\&\quad\times\langle P_\lambda|P_{\lambda''}\rangle\,\langle P_{\lambda'}|(K+e_\gamma-E)|\xi_p\rangle=0,\end{aligned}$$

where now it vanishes only due to the tridiagonal nature of the $J^\gamma_{pp'}$ matrix

$$\langle P_\lambda|(K+e_\gamma-E)|\xi_p\rangle=0,\quad p\geqslant N,\quad 1\leqslant\lambda\leqslant N_t.$$

Using Eqs. (3) and (15), and (47) is further reduced to

$$\begin{aligned}\langle\Psi^\Gamma_i|H-E|\Psi^\Gamma_{\gamma p}\rangle&\approx\sum_{\lambda=1}^{N}\sum_{p'=0}^{N-1}C^\Gamma_{i\gamma\lambda}D_{\lambda p'}J^\gamma_{p'p}\\&=\delta_{pN}\sum_{\lambda=1}^{N}C^\Gamma_{i\gamma\lambda}D_{\lambda,N-1}J^\gamma_{N-1,N},\end{aligned}$$

deriving X^γ_i in form conveniently identical to the the one-electron target's X^γ_i [7]:

$$X^\gamma_i=\sum_{\lambda=N_t+1}^{N}C^\Gamma_{i\gamma\lambda}D_{\lambda,N-1}.\tag{48}$$

Being constrained by the Fano's subshell structure of the many-electron matrix elements from the corresponding preceding section, Eq. (16) could not be used to calculate the $C^\Gamma_{i\gamma\lambda}$ coefficients directly. If, however, Eq. (16) is viewed as the definition of $C^\Gamma_{i\gamma\lambda}$, then

$$C^\Gamma_{i\gamma\lambda}=\langle\Psi^\Gamma_{\gamma\lambda}|\Psi^\Gamma_i\rangle,\tag{49}$$

where the $(a+1)$-electron eigenstates $\{\Psi^\Gamma_i\}$ are obtained from the subshell-structured $(a+1)$-electron basis $\{\Phi^\Gamma_j\}$ via

$$\begin{aligned}\langle\Psi^\Gamma_i|H|\Psi^\Gamma_{i'}\rangle=E_i\delta_{ii'},\quad\langle\Psi_i|\Psi_{i'}\rangle=\delta_{ii'},\\|\Psi^\Gamma_i\rangle=\sum_j C_{ij}|\hat{A}\Phi^\Gamma_j\rangle.\end{aligned}\tag{50}$$

In the notation of Eqs. (6), (7), and (8), the Φ^Γ_j functions are specified as

$$\begin{aligned}|\Phi^\Gamma_j\rangle&\equiv|\mathbf{a}_j\mathbf{s}_j\mathbf{S}_j\mu_\Gamma\rangle,\\\mathbf{a}_j&=(a_{j1},a_{j2},\ldots,a_{jN}),\\\mathbf{s}_j&=(s_{j1},s_{j2},\ldots,s_{jN}),\\\mathbf{S}_j&=(S_{j1}\equiv s_{j1},S_{j2},\ldots,S_{jN}\equiv S_\Gamma),\\\sum_{\lambda'=1}^{N}a_{j\lambda'}&=a+1,\qquad\sum_{\lambda'=N_t+1}^{N}a_{j\lambda'}\leqslant 1,\end{aligned}\tag{51}$$

where the last summation says that the subshell structure of every Φ^Γ_j should not include more than one electron in the *transitional* Eq. (15) subshells ensuring that $\{\Phi^\Gamma_j\}$ covers identical $(a+1)$-electron functional space when comparing to $\{\Phi^\Gamma_{\gamma\lambda}\}_{\lambda=1}^N$ [Eq. (14)].

For the required $\lambda=N_t+1,\ldots,N$ [Eq. (48)], the final expression for $C^\Gamma_{i\gamma\lambda}$ could now be reduced further with the aid of Eqs. (10), (11), and (50) arriving at

$$\begin{aligned}C^\Gamma_{i\gamma\lambda}&=\sum_j\sum_\beta C^t_{\gamma\beta}C_{ij}\langle\hat{A}\phi^\Gamma_\beta P_\lambda|\hat{A}\Phi^\Gamma_j\rangle\\&=\sum_\beta C^t_{\gamma\beta}C_{i,j=\{\beta\lambda\}}.\end{aligned}\tag{52}$$

Since $N_t < \lambda \leqslant N$, for every required configuration $|\phi_\beta^\Gamma P_\lambda\rangle$, there should exist a corresponding $(a+1)$-electron basis function $|\Phi_j^\Gamma\rangle$ such that

$$\begin{aligned} \mathbf{a}_j &= (a_{\beta 1}, a_{\beta 2}, \ldots, a_{\beta N_t}, a_\lambda), \quad a_\lambda \equiv 1 \\ \mathbf{s}_j &= (s_{\beta 1}, s_{\beta 2}, \ldots, s_{\beta N_t}, s_\lambda), \quad s_\lambda = s \equiv \tfrac{1}{2} \\ \mathbf{S}_j &= (S_{\beta 1}, S_{\beta 2}, \ldots, S_{\beta N_t}, S_\Gamma), \end{aligned} \tag{53}$$

where the $N_t + 1$'s places are used for the only remaining nonempty subshell.

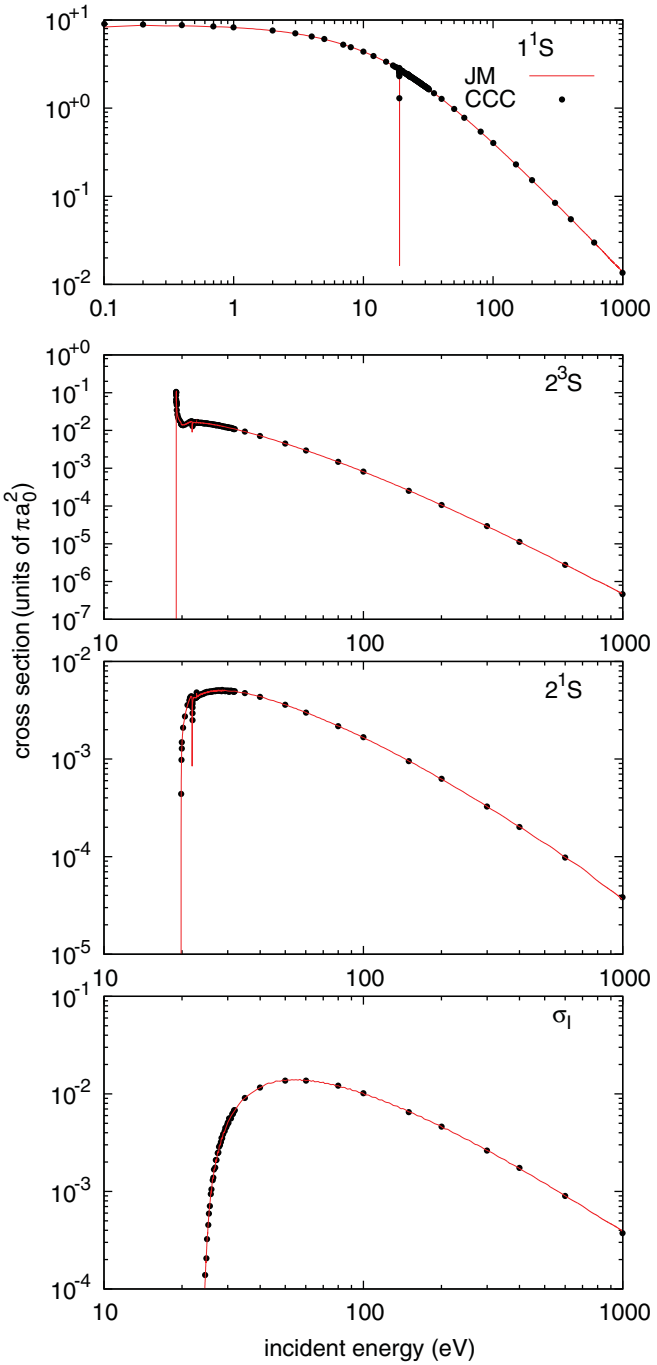

FIG. 1. (Color online) Elastic, single-excitation, and ionization cross sections (πa_0^2) for electron scattering on a ground-state helium target in the frozen-core S-wave model.

III. RESULTS

The original JM functions [3,29] are used in this study, while the complete set of equations relevant to the S-wave JM scattering could be found in [7]. The Laguerre exponential falloff was fixed at $\lambda_L = 2$. For conversion purposes, one atomic unit of energy (or Hartree) was set to 27.211 383 86 eV as per the latest recommended values at the time of publication [30]. A tabular form of the JM and CCC results (Figs. 1 and 2) is available [24].

Our immediate goal is to solve the S-wave model of e-He scattering in full, which includes ionization-plus-excitation and double-ionization processes. Before this could be attempted, it is essential to thoroughly test the JM implementation of e-He scattering. To do so, we use the well-established CCC method [31] to obtain benchmark results across an energy range from 0.1 to 1000 eV, paying particular attention to the resonance regions, as these have not been detailed previously.

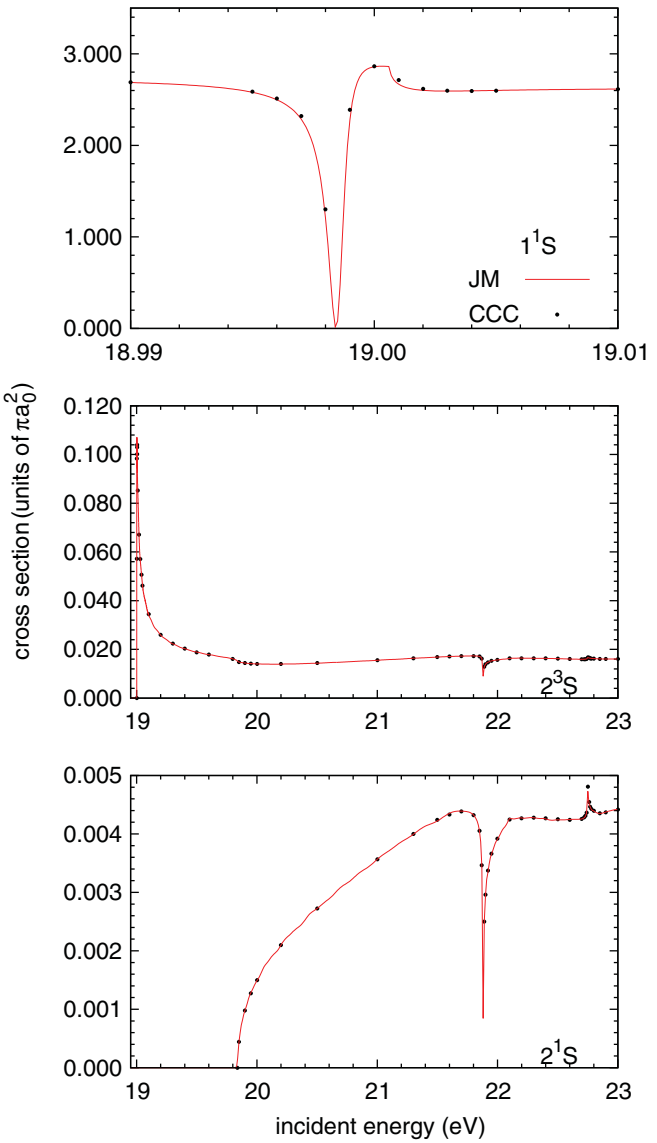

FIG. 2. (Color online) The same as in Fig. 1 but with focus on the resonances.

The CCC method has been used with a number of different L^2 basis functions. To guide the choice of the JM calculation parameters and to make comparison between the JM and CCC results as direct as possible, the helium target states are created identically in both methods. This is accomplished in the following steps: (i) create N_t orthogonal Laguerre functions (see [7] for details); (ii) diagonalize the helium-ion (He^+) one-electron Hamiltonian (4); (iii) create all possible singlet (N_t) and triplet ($N_t - 1$) two-electron configurations, where one electron always occupies the $1s$ eigenstate of He^+; (iv) diagonalize the helium Hamiltonian on this basis obtaining two-electron helium (target) states. In our case, with $N_t = 50$, the ground-state eigenvalue is $e(1s^2, {}^1S) = -2.872\,506\,9$.

Convergence in the CCC cross sections was achieved at $N_t = 50$ by increasing the number of expansion states by 10 at every energy calculated until there was no visible difference between consecutive calculations at any energy, with only $N_t = 50$ results presented in Figs. 1 and 2. Having an identical atomic target model in both CCC and JM methods provides a unique opportunity to study convergence in the JM method. It is important to emphasize here that, given the identical target model, the only difference between the JM and CCC results will be due to the outer-region approximation of the JM method, which is controlled by the single parameter N. In theory, the JM results should converge to the CCC results as N increases.

It was found that $N = 81$ was sufficient to reproduce the CCC results for the complete energy range from 0.1 to 1000 eV. The presented JM results in Figs. 1 and 2 were calculated on a laptop with 2.2-GHz CPU and 3.5-GB RAM taking about five hours to complete at more than 4000 considered energy points. The following JM computational values were used (see [7] for explanation of the parameters): $N_t = 50, N = 81, \ln(c) = -7$, $r_{\max} = 450$, $M_{\mathrm{LCR}} = 1601$, where the radial grid was between zero and $r_{\max}$ and M_{LCR} is the number of equally spaced points in the radial LCR grid [7].

The agreement between JM and CCC results is excellent for elastic scattering, excitation, and ionization Eq. (23). It will be a major challenge to obtain convergent total ionization cross sections for the case where the residual ion is left in an excited state, or when autoionizing doubly excited states are incorporated by removing the frozen-core (FC) approximation.

IV. CONCLUSIONS

We have extended the JM method to many-electron target systems, where the presented formalism is fully integrated with Fano's [25] many-configuration matrix elements. Note that, even though the method was applied in the frozen-core S-wave model, the described JM formulation is completely generic in terms of permissible electron configurations. Such a formulation will be required in our future attempt to solve the S-wave model exactly without the FC approximation.

Comparison of the JM and CCC results demonstrated that the JM method is very accurate and computationally highly efficient. In particular, the JM results are in exact agreement with the CCC results between 0.1 and 1000 eV. Note that the JM results were obtained with the same set of calculation parameters for the entire energy region spanning four orders of magnitude, that is, no further adjustments were made for any particular energy region. Therefore, arguably, the JM method joins the CCC method in being one of the very few *ab initio* scattering methods capable of a uniform treatment of electron scattering across a broad energy range.

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[1] E. J. Heller and H. A. Yamani, Phys. Rev. A **9**, 1201 (1974).
[2] E. J. Heller and H. A. Yamani, Phys. Rev. A **9**, 1209 (1974).
[3] J. Broad and W. Reinhardt, J. Phys. B: At Mol. Phys. **9**, 1491 (1976).
[4] D. A. Konovalov and I. E. McCarthy, J. Phys. B: At. Mol. Opt. Phys. **27**, L407 (1994).
[5] D. A. Konovalov and I. E. McCarthy, J. Phys. B: At. Mol. Opt. Phys. **27**, L741 (1994).
[6] D. A. Konovalov and I. E. McCarthy, J. Phys. B: At. Mol. Opt. Phys. **28**, L139 (1995).
[7] D. A. Konovalov and I. Bray, Phys. Rev. A **82**, 022708 (2010).
[8] A. Temkin, Phys. Rev. **126**, 130 (1962).
[9] R. Poet, J. Phys. B: At. Mol. Phys. **11**, 3081 (1978).
[10] S. Jones and A. T. Stelbovics, Phys. Rev. A **66**, 032717 (2002).
[11] S. Jones and A. T. Stelbovics, Phys. Rev. Lett. **84**, 1878 (2000).
[12] M. Baertschy, T. N. Rescigno, W. A. Isaacs, and C. W. McCurdy, Phys. Rev. A **60**, R13 (1999).
[13] A. L. Frapiccini, J. M. Randazzo, G. Gasaneo, and F. D. Colavecchia, J. Phys. B: At. Mol. Opt. Phys. **43**, 101001 (2010).
[14] M. Draeger, G. Handke, W. Ihra, and H. Friedrich, Phys. Rev. A **50**, 3793 (1994).
[15] M. S. Pindzola, D. Mitnik, and F. Robicheaux, Phys. Rev. A **59**, 4390 (1999).
[16] C. Plottke, I. Bray, D. V. Fursa, and A. T. Stelbovics, Phys. Rev. A **65**, 032701 (2002).
[17] C. Plottke, P. Nicol, I. Bray, D. V. Fursa, and A. T. Stelbovics, J. Phys. B: At. Mol. Opt. Phys. **37**, 3711 (2004).
[18] D. A. Horner, C. W. McCurdy, and T. N. Rescigno, Phys. Rev. A **71**, 010701(R) (2005).
[19] D. A. Horner, C. W. McCurdy, and T. N. Rescigno, Phys. Rev. A **71**, 012701 (2005).
[20] P. L. Bartlett and A. T. Stelbovics, Phys. Rev. A **81**, 022715 (2010).
[21] P. L. Bartlett and A. T. Stelbovics, Phys. Rev. A **81**, 022716 (2010).

[22] P. G. Burke and W. D. Robb, Adv. At. Mol. Phys. **11**, 143 (1975).
[23] I. Bray and A. T. Stelbovics, Adv. At. Mol. Phys. **35**, 209 (1995).
[24] The complete Java source code used in this study is freely available from jmatrix.googlecode.com or a relevant link at [www.dmitrykonovalov.org] for academic use.
[25] U. Fano, Phys. Rev. **140**, A67 (1965).
[26] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).
[27] H. A. Yamani, A. D. Alhaidari, and M. S. Abdelmonem, Phys. Rev. A **64**, 042703 (2001).
[28] B. W. Shore, Phys. Rev. **139**, A1042 (1965).
[29] H. A. Yamani and L. Fishman, J. Math. Phys. **16**, 410 (1975).
[30] P. J. Mohr, B. N. Taylor, and D. B. Newell, Rev. Mod. Phys. **80**, 633 (2008).
[31] D. V. Fursa and I. Bray, Phys. Rev. A **52**, 1279 (1995).