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# Theory and computation of triply excited resonances: Application to states of He$^-$

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Autoionizing multiply excited states offer unusual challenges to the theory of electronic structure and spectra because of the presence of strong electron correlations, of their occasional weak binding, of their proximity to more than one threshold, and of their degeneracy with many continua. Here we discuss a theory that addresses these difficulties in conjunction with the computation of their wave functions and intrinsic properties. Emphasis is given on the justification of the possible presence of self-consistently obtained open-channel-like (OCL) correlating configurations in the square-integrable representation of such states and on their effect on the energy $E$ and the width $\Gamma$. Application of the theory has allowed the prediction of two hitherto unknown He$^-$ triply excited resonances, the $2s2p^2\,{}^2P$ ($E=59.71$ eV, above the He ground state, $\Gamma=79$ meV) and the $2p^3\,{}^2D^o$ ($E=59.46$ eV, $\Gamma=282$ meV) (1 a.u.$=27.2116$ eV). These resonances are above the singly excited states of He and are embedded in its doubly excited spectrum. The relatively broad $2p^3\,{}^2D^o$ state interacts strongly with the He $2s2p\,{}^3P^o\,\epsilon d$ continuum. The effect of this interaction has been studied in terms of the coupling with fixed core scattering states as well as with a self-consistently computed OCL bound configuration. The position of the He$^-$ $2p^3\,{}^2D^o$ resonance is below that of the He $2p^2\,{}^1D$ autoionizing state at 59.91 eV and of the He $2p^2\,{}^3P$ bound state at 59.68 eV. The partial decay widths to the three important open channels are $\gamma(2s2p\,{}^3P^o)=252$ meV, $\gamma(1s2p\,{}^3P^o)=21$ meV, $\gamma(1s2p\,{}^1P^o)=9$ meV. The final core states are also represented by correlated (multiconfigurational Hartree-Fock) functions. The $2s2p^2\,{}^2P$ state couples to four neighboring He thresholds, the $2s2p\,{}^3P^o$, $2p^2\,{}^3P$, ${}^1D$, and $2s2p\,{}^1P^o$. It is above the He $2s2p\,{}^3P^o$ threshold at 58.31 eV, with respect to which it is a valence shape resonance, and below the He $2p^2\,{}^1D$ and $2s2p\,{}^1P^o$ autoionizing states. In the limit of an exact energy calculation, we suggest that its position would also come below that of the $2p^2\,{}^3P$ state, which it overlaps. Its partial widths are $\gamma(2s2p\,{}^3P^o)=60$ meV, $\gamma(1s2p\,{}^3P^o)=9$ meV, $\gamma(1s2p\,{}^1P^o)=10$ meV. The present results, considered together with published ones on other $n=2$ intrashell states, show that the recently measured [R. N. Gosselin and P. Marmet, Phys. Rev. A **41**, 1335 (1990)] closely lying structures at 58.415 and 58.48 eV cannot correspond to the He$^-$ $2p^3\,{}^4S^o$ and ${}^2D^o$ states, as these authors proposed.

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## I. INTRODUCTION

In a recent publication, Gosselin and Marmet [1] presented new results from high-resolution measurements of He$^-$ triply excited resonances. They observed and analyzed the well-known He$^-$ $2s2p^2\,{}^2D$ resonance at $58.283\pm0.003$ eV as well as two "previously unknown structures" at $58.415\pm0.005$ and $58.48\pm0.02$ eV. By making the analogy with states of the carbon atom, Gosselin and Marmet identified these peaks with the He$^-$ $2p^3\,{}^4S^o$ and $2p^3\,{}^2D^o$ states, respectively.

In the present paper we show that this assignment is incorrect. This conclusion follows from a review of the existing literature on He$^-$ $n=2$ triply excited states (TES's) and from the results of new calculations. These calculations—whose theoretical justification is the subject of Secs. III and IV—incorporate the effects of electron correlation and have allowed the prediction of the positions and the partial and total widths of the hitherto unknown triply excited He$^-$ resonances, $2s2p^2\,{}^2P$ ($E=59.71$ eV, $\Gamma=79$ meV) and $2p^3\,{}^2D^o$ ($E=59.46$ eV, $\Gamma=282$ meV). [The conversion to eV above the He $1s^2\,{}^1S$ ground state is done using $E(\text{He})=-2.903\,72$ a.u., 1 a.u.$=27.2116$ eV.]

The above two new He$^-$ resonances are interesting in many ways and have given us the opportunity to study and discuss aspects of the theory and computation of localized states which belong to the continuous spectrum and mix with open channels, and which are heavily correlated, polyelectronic (i.e., with more than two electrons), and quasibound in a weak (negative-ion) potential. Both constitute prototypical examples of two categories of resonances: The He$^-$ $2p^3\,{}^2D^o$ state is a closed-channel (Feshbach) resonance with respect to two thresholds, mixing heavily with the (He $2s2p\,{}^3P^o$)$\epsilon d$ open channel (due to the strong $2p^2\leftrightarrow 2s\epsilon d$ coupling) and lightly with the (He $1s2p\,{}^{3,1}P^o$)$\epsilon d$ channels (due to the relatively weak $2p^2\leftrightarrow 1s\epsilon d$ coupling). The He$^-$ $2s2p^2\,{}^2P$ state couples to four neighboring thresholds of He doubly excited states. It is a shape resonance with respect to He $2s2p\,{}^3P^o$ at 58.31 eV, into which it decays. Its localization and subsequent autoionization are essentially the results of the difference between state-specific self-consistent fields of the initial ($2s2p^2$) and final ($2s2p\,{}^3P^0\epsilon p$) states. Finally, the He$^-$ $2s2p^2\,{}^2P$ resonance is below the He $2p^2\,{}^1D$ and $2s2p\,{}^1P^o$ thresholds. Although our computation placed it

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above the $2p^2\,{}^3P$ bound state by 0.025 eV, we predict that its exact position is just below, i.e., it is a Feshbach resonance with respect to this threshold as well.

## II. KNOWN $n=2$ TRIPLY EXCITED STATES OF He$^-$

Since the early 1960s, the He$^-$ spectrum has served as a testing ground for theoretical as well as experimental methods for the study of resonances. In this section, we review briefly some of the existing information on the energies and widths of the $n=2$ TES's of He$^-$ as this relates to the identifications of Ref. [1].

The He$^-$ $2p^3\,{}^4S^o$ state is a bound (discrete) state and not a resonance [2–4]. Its energy is known from theory as being around 59.33 eV above the ground state [3,4] and, in fact, it was recently identified experimentally [5] from the predicted characteristic property of its radiative decay to the He $1s2p\,{}^3P^o+e^-$ continuum [3,4].

As regards the $2s2p^2\,{}^2D$ resonance, a very timely finding of the new measurements [1] is that they placed it 29 meV *below* the position of the He $2s2p\,{}^3P^o$ resonance, ($E=58.309\pm0.003$ eV). In other words, it is a closed-channel (Feshbach) resonance with respect to this threshold. This finding should be added as an element to the recent debate [6,7] on the theory and understanding of resonances and on appropriate methods for their computation. In an earlier paper [8], Chung and Davis had disputed the original Fano and Cooper resonance assignment and had concluded that "what has been seen in the experiment could be the result of a postcollision interaction effect." In his latest comment on the observed structure at 58.3 eV, Chung states (see Ref. [7], p. 695) that his calculation "ruled out the possibility that this ${}^2D$ structure is a Feshbach resonance lying below the $2s2p\,{}^3P^o$ threshold." This statement is now in contradiction with the recent experiment [1]. On the other hand, our position has been that the fundamental criterion for understanding and for determining the existence of an $N$-electron resonance is the direct or indirect manifestation of its *localization.* In the case of the He$^-$ ${}^2D$ structure, it represents a resonance regardless of whether it is above or below the $2s2p\,{}^3P^o$ threshold, and this is because there exist appropriate multiconfigurational Hartree-Fock (MCHF) solutions representing its localized part in zeroth order. Knowledge of the energy of the He$^-$ $2s2p^2\,{}^2D$ state relative to the He $2s2p\,{}^3P^o$ threshold is necessary not because one has to call it a "Feshbach" resonance or not (anyway, it is already below another threshold, the He $2p^2\,{}^1D$ resonance at 59.91 eV), but because one has to know which channels are open and which are closed when studying the decay dynamics or when computing the total and the partial widths (see, e.g., [9]).

Let us now turn to four more states, $2s^22p\,{}^2P^o$, $2s2p^2\,{}^4P$, $2s2p^2\,{}^2S$, and $2p^3\,{}^2P^o$. The established $2s^22p\,{}^2P^o$ resonance at 57.22 eV [10] is outside the present range of interest. For the $2s2p^2\,{}^4P$ resonance, large-scale computations [8], which, however, did not account for the energy shift due to explicit coupling with the continuum, have produced an energy of 57.42 eV. A recent computation of the complex energy of this state [6] has obtained an energy shift $\Delta=0.027$ eV and a width $\Gamma=0.015$ eV.

The information on the $2s2p^2\,{}^2S$ resonance is less definitive. It has been assigned to experimental peaks from scattering experiments, by Grissom, Compton, and Garrett [11] at 58.8 or 59.4 eV, by Spence [12] at 59.0 eV, and by van der Burgt, van Eck, and Heidemann [13] at 59.90 eV with a width of 400±100 meV. On the theoretical side, the early close-coupling calculations of Ormonde, Kets, and Heidemann [14] predicted it to be at 59.4 eV with a width of $\Gamma=300$ meV, while Nesbet [15], using the stabilization method, computed an energy of 59.32 eV after he shifted it downward by 0.2 eV, which was the difference between his computed energy for the $2s^22p\,{}^2P^o$ state and the exact one ($E=57.22$ eV). On the other hand, Ahmed and Lipsky [16] used the model of truncated diagonalization with hydrogenic basis sets and obtained four roots of ${}^2S$ symmetry in the range 58.07–59.61 eV. However, such a fixed basis calculation of energies cannot resolve the question of the existence of corresponding resonances.

Finally, the He$^-$ $2p^3\,{}^2P^o$ resonance has been placed at about 60.5 eV by Nicolaides and Beck [17] and at 60.43 eV by Nesbet [15] (after the downward shift of 0.2 eV). Both computations used only bound wave functions. In our case [17], by including the strongly mixing open-channel-like (OCL) configurations $2s2p3d$ in the Hamiltonian matrix (see later sections), it was possible to predict the approximate positions of two higher-lying resonances as well.

The facts given above do not allow the identification of the new peaks [1] with any of the known $n=2$ triply excited He$^-$ resonances. Therefore we decided to complete the picture of the He$^-$ $n=2$ resonances by computing the energies and widths corresponding to the two as yet unexamined configurations, the $2s2p^2\,{}^2P$ and the $2p^3\,{}^2D^o$.

## III. THEORY

The present analysis and calculations have been carried out in the framework of a theoretical approach to autoionizing states which combines electronic structure theory with the properties of decay states [6,9,18–26]. For the intrinsic properties of energy and width which are studied here, a two-step methodology is followed. The first step aims at the computation of the localized part of the resonance, in a justified manner which incorporates highly developed methods for the computation of arbitrary electronic structures. The second step aims at the subsequent incorporation of the remaining effects of the multichannel continuum. The salient features of the theory are as follows.

Rather than looking for definitions and rigorous representations of projection operators as required by the well-known Feshbach resonance-scattering theory (see, e.g., [27]), the foundations of the present approach use the fact of the dependence of the solutions of the Schrödinger equation on the asymptotic boundary conditions. From this point of view, autoionizing states are represented by nonsquare-integrable wave functions satisfying a complex eigenvalue Schrödinger equation. Imposition of square-integrability boundary conditions results in a real eigenvalue problem of an effective Hamiltonian $H_0=QHQ$, $Q=|\Psi_0\rangle\langle\Psi_0|$, $H_0\Psi_0=E_0\Psi_0$, where $H$ is the exact Hamiltonian, $\Psi_0$ is square integrable, and $E_0$ is real. The consequence of this change in boundary conditions is the appearance of a small energy shift $\Delta$.

When requiring the solution of the multielectron Schrödinger equation to be square integrable with a real eigenvalue embedded in the continuous spectrum, concern as to the computational method and the choice of function spaces ought to arise, as well as considerations of the theory's general applicability regarding electronic structure and number of electrons. Starting with the work of [18], this problem has been tackled by recognizing the advantages of the state-specific HF or MCHF wave function as regards the possibility of representing efficiently and reliably the results of the dynamically self-adjusting major correlations contribution to localization. Thus the localized part of the autoionizing state of any type of electronic structure is represented by

$$\Psi_0=\Phi_{\mathrm{MCHF}}+X_{\mathrm{loc}}\ , \quad \langle\Phi_{\mathrm{MCHF}}|X_{\mathrm{loc}}\rangle=0\ , \tag{1}$$

where $X_{\mathrm{loc}}$ represents the remaining localized correlations contributing to the stability of the state. When necessary, by construction and/or by core orbital orthogonalization, $X_{\mathrm{loc}}$ excludes selectively lower-lying states of the same symmetry. On the other hand, this is not always done for the MCHF solution, since it is sometimes the very structure of the MCHF equations that requires the presence of specific lower-lying configurations in order for convergence to occur. [E.g., in Ref. [19], in order to obtain the $\mathrm{He}^-$ $1s2s2p\ ^2P^o$ solution, the coupling $1s(2s2p)\ ^{3,1}P^o$ rather than $(1s2s)\ ^{3,1}S2p$ was adopted and the $1s^22p\ ^2P^o$ configuration was included.] Furthermore, as it is explained in the following sections, the correlating bound configurations which are chosen to enter $\Phi_{\mathrm{MCHF}}$ or $\Psi_0$ may or may not correspond to the structure of the open channels, depending on the possibility or reliability of convergence of the $\Phi_{\mathrm{MCHF}}$ solution and on the properties that must be computed.

Having obtained $\Psi_0$ and $E_0$, the partial and the total energy shifts and widths are computed either from the solution of complex eigenvalue equations of appropriate non-Hermitian matrices constructed from bound functions only [6,9,24], or from the solution of the defining equation for resonances in the complex energy plane, which emerges when they are treated as decaying states [18]:

$$z-E_0-\Delta(z)+\frac{i}{2}\Gamma(z)=0\ , \quad z \text{ complex}\ . \tag{2}$$

In this case, the problem is how to choose and manipulate bound as well as $N$-electron, term-dependent, energy-normalized scattering functions $U(\mathcal{E})$.

In this work, it is the second method that we have applied. Thus, given the smallness of $\Delta(z)$ and $\Gamma(z)$ for autoionizing states, first the real part of Eq. (2) is evaluated for $\mathrm{Re}z=\mathcal{E}$ for each open channel $i$ separately. This independent channel approximation (ICA) is justified by the structure of the thresholds of the present problem. (For all-order interchannel coupling calculations, see Refs. [9,19,20,24].) The resulting expression that must be solved for an isolated resonance is

$$\mathcal{E}-E_0-\delta_i(\mathcal{E})=0\ , \tag{3a}$$

$$\delta_i(\mathcal{E})=\mathrm{P}\int_{E_i}\frac{|\langle\Psi_0|H-\mathcal{E}|U_i(\varepsilon)\rangle|^2}{\mathcal{E}-\varepsilon}d\varepsilon\ , \tag{3b}$$

(P denotes principal value, $\varepsilon$ the energy variable, and $E_i$ the threshold energy). The operator $(H-\mathcal{E})$, rather than $H$, is necessary in practice due to the nonorthonormality between the separately computed function spaces representing $\Psi_0$ and $U_i(\varepsilon)$. Having obtained all the $\delta_i$, the total energy shift and total energy $E$ are given by

$$\Delta=\sum_i\delta_i\ , \quad E=E_0+\Delta\ . \tag{4}$$

We note that finding the root of Eq. (3a) rather than the direct evaluation of Eq. (3b) for a fixed $\mathcal{E}=E_0$ is more appropriate for any strongly interacting channel since, in this case, the shift and width are in principle energy dependent.

Finally, given that for the challenging TES's of negative ions very little is known about their decay dynamics, we have used two expressions for the computation of the partial widths. The first,

$$\gamma_i(E_0)=2\pi|\langle\Psi_0|H-E_0|U_i(E_0)\rangle|^2\ , \tag{5}$$

is evaluated at $E_0$ and represents the golden rule for the autoionization probability. The second,

$$\gamma_i(E)=\frac{2\pi|\langle\Psi_0|H-E|U_i(E)\rangle|^2}{1-\delta_i'(E)}\ , \tag{6a}$$

is evaluated at $E$ [Eq. (4)], while its denominator contains the derivative of the energy shift at $E$. This denominator is the well-known correction for the energy dependence of the width [27]. Equation (6a) is also derived and discussed in Sec. V, in connection with the question of choice of $\Psi_0$ and in particular of the inclusion of OCL correlating configurations in the $\Phi_{\mathrm{MCHF}}$ of $\Psi_0$. The total width is given by

$$\Gamma=\sum_i\gamma_i\ . \tag{6b}$$

In the above expressions, $U_i(E)$ is a symmetry-adapted product of a term-dependent correlated core wave function $\Psi_i$ and a scattering orbital $\varphi_i(E-E_i)$, where $E_i$ is the threshold energy for channel $i$ and $E-E_i$ is the energy of the free electron. $\varphi_i(E-E_i)$ is computed in the fixed core HF approximation.

## IV. LOCALIZATION, INTERPRETATION OF THE MCHF SOLUTIONS, AND BOUND WAVE FUNCTIONS OF STATES EMBEDDED IN THE CONTINUUM

The strategy of initializing the calculation of autoionizing states with a state-specific MCHF wave function allows the major configurational features of a multiply excited state (MES) to emerge clearly and quantitatively while the MCHF energy is reasonably close to $E_0$. This implies that, for many problems, physically significant results can be obtained without computing $X_{\rm loc}$, which is indeed considered only when high accuracy is required. For example, consider the triply excited He$^-$ $2s2p^2\,{}^4P$ resonance [6]. A three-term MCHF calculation with the He$^+$ 1$s$ orthogonality imposed on it yields

$$\Phi_{\rm MCHF}({}^4P)=0.990(2s2p^2)+0.105(2p^23d)$$
$$-0.092(2s3d^2)\ , \tag{7}$$

whose energy $E_{\rm MCHF}=-0.785\,21$ a.u. ($=57.648$ eV above He $1s^2\,{}^1S$) is only about 0.25 eV above the values obtained from large-scale computations [8]. Going beyond $\Phi_{\rm MCHF}({}^4P)$ in terms of only seven additional, variationally optimized virtual orbitals yields a compact $\Psi_0$ with $E_0=57.414$ eV, in agreement with the results of [8]. Such a rapid convergence of suitably chosen MCHF solutions for MES's has been observed in a number of applications, such as the analysis of wave functions and of geometric properties [20,22,23] and the computation of positions and widths of broad resonances such as the He$^-$ $1s2s2p\,{}^2P^o$ [19], of valence shape resonances such as the He$^-$ $1s2p^2\,{}^4P$ and ${}^2P$ [3], of multichannel resonances [9], of doubly excited states [21], and of inner hole states [24], or of the effect of coupling to an external ac or dc field [26].

For the present work, similar efficiencies in accounting for the major electron correlation effects when optimizing the Fermi-Sea configurations self-consistently have been observed. For example, for the He $2s2p\,{}^3P^o$ state, which is one of the final core states into which the herein studied He$^-$ resonances decay, a three-term MCHF solution, with He$^+$ 1$s$ orthogonality constraint, produces the following:

$$\begin{aligned}\Phi_{\rm MCHF}({}^3P^o)&=0.992(2s2p)-0.118(2p3d)\\&\quad-0.049(3s3p)\ ,\\E_{\rm MCHF}({}^3P^o)&=-0.760\,93\ \text{a.u.}\\&=58.309\ \text{eV above He}\ {}^1S\ .\end{aligned} \tag{8}$$

The remaining localized and asymptotic correlation add to a very small shift. The recent experiment [1] has measured $E=58.309\pm0.003$ eV.

Having mentioned the good accuracy exhibited by calculations of MES's using compact MCHF wave functions, it is appropriate to point out that, not surprisingly, straightforward and physically meaningful convergence is sometimes difficult—if not impossible—to achieve. This difficulty is due to the open-shell character of the contributing configurations to near-degeneracies, or to weak binding potentials, and may lead to positive energy orbitals, or to oscillatory solutions or to "solutions" for which the average radius of an orbital is unphysically large. A practical remedy for such cases that is often successful is to use nonorthonormal configurations or suitable orbital rotations which eliminate troublesome single orbital excitations.

Finally, we elaborate on the question of the presence in $\Phi_{\rm MCHF}$ of correlating configurations whose structure is the same as that of open channels. This question was part of the recent debate [6,7] on the computation of resonances, using as a test case the triply excited $2s2p^2\,{}^2D$ resonance of He$^-$.

Let us take again the He$^-$ $2s2p^2\,{}^2D$ resonance. This state, whose width is abut 60 meV, is located 0.45 eV above the He $2s^2\,{}^1S$ threshold and overlaps the He $2s2p\,{}^3P^o$ resonance, whose width is about 8 meV [1,10].

If we consider, beyond the single configuration, the correlation of the $2p^2$ electrons, then this gives rise to the important orbital rearrangement (among other virtual excitations)

$$2p^2\leftrightarrow 2sd\ , \tag{9}$$

where $d$ is a one-electron function of $l=2$ symmetry, which can be written formally as a sum over a complete set of orbitals [see Eq. (46) of Ref. [18]]. In the case of He$^-$ $2s2p^2\,{}^2D$, what emerges from (9) is a correlating configuration, $2s^2d$, which has the same structure as that of the open channel $2s^2\,{}^1S\epsilon d$, into which the $2s2p^2\,{}^2D$ configuration (and state) is embedded. The same situation arises in the case of the $2p^3\,{}^2D^o$ He$^-$ resonance studied here, where the open channel is the $2s2p\,{}^3P^o\epsilon d$ (the $2s2p\,{}^1P^o\epsilon d$ channel is closed). Thus the $d$ function of (9) represents the integral over the scattering orbitals $\epsilon d$. The question then is, if convergence of MCHF or variational calculations is achieved for the $2s2p^2\,{}^2D$ or $2p^3\,{}^2D^o$ states (and many similar ones) with a $2s^23d$ configuration (or a $2s2p3d$ for the ${}^2D^o$ state) present, how is the result to be interpreted? Our answer is that the "$3d$" function has incorporated the contribution from that part of the continuous spectrum which contributes to *dynamical localization,* i.e., to a square-integrable $\Psi_0$ whose important zeroth-order orbitals account to a good approximation for the interaction with the continuum. *Thus, for such a* $\Psi_0$, *a large part of the energy shift due to discrete-continuum interaction is already in* $E_0$. Let us elaborate by analyzing a hierarchy of wave functions for the He$^-$ $2s2p^2\,{}^2D$ resonance, starting from the hydrogenic (interactionless) zeroth-order model.

Consider the single configuration HF solution for He$^-$ $2s2p^2\,{}^2D$. Its energy ($E_{\rm HF}=-0.707\,72$ a.u.) is in the continuous spectrum He $2s2p\,{}^3P^o+e^-$. (The experimental energy of He $2s2p\,{}^3P^o$ is $-0.761$ a.u.) Yet, it exists as a square-integrable function which has been obtained rigorously by solving shell-dependent integrodifferential equations and did not collapse to the He $2s2p\,{}^3P^o$ threshold. What is happening?

Assume the hydrogenic interactionless model. Call $|m\rangle$ the multiply excited $N$-electron hydrogenic state of interest which is embedded as a discrete state in the $N$-electron hydrogenic continuous spectrum $|\varepsilon\rangle$. Let $|n\rangle$ be the set of the discrete, $N$-electron hydrogenic solutions. Now introduce the interelectronic interaction operator. Then, to lowest order, the perturbed wave function is given by

$$\Psi_m = |m\rangle + \sum_{\substack{n,m\\ n\neq m}} \frac{|n\rangle\langle m|H|n\rangle}{\varepsilon_m-\varepsilon_n} + \int d\varepsilon \frac{|\varepsilon\rangle\langle m|H|\varepsilon\rangle}{\varepsilon_m-\varepsilon} + \cdots . \tag{10}$$

It is the singularity in the integral for $\varepsilon_m = \varepsilon$ that converts the hydrogenic bound function $|m\rangle$ into a correlated unbound function. However, if we exclude a small part of the continuous spectrum around $\varepsilon_m \pm \delta$ as a principal-value integral, $\Psi_m$ becomes square-integrable because the terms

$$\int_{-\infty}^{\varepsilon_m-\delta} d\varepsilon \frac{|\langle m|H|\varepsilon\rangle|^2}{\varepsilon_m-\varepsilon} \quad \text{and} \quad \int_{\varepsilon_m+\delta}^{+\infty} d\varepsilon \frac{|\langle m|H|\varepsilon\rangle|^2}{\varepsilon_m-\varepsilon} \tag{11}$$

are finite.

Given a configuration, the HF model goes beyond the interactionless hydrogenic one in that it includes the interaction self-consistently. In the present context, achieving the HF solution of the $\text{He}^-$ $2s2p^{2}\,{}^2D$ configuration means that, for this state, the HF valence structure essentially determines intrinsically a cutoff $\delta$ such that the hydrogenic $\epsilon p$ contributions to the ${}^2D$ HF $2p$ orbital come from the finite integrals (11). As the (formally introduced) cutoff parameter $\delta$ decreases and the singularity is approached, one of the orbitals becomes increasingly diffuse.

If now we replace the hydrogenic $|m\rangle$ in Eq. (10) by the HF function, which we know is bound, and the remaining vectors $|n\rangle$ by correlating configurations, a similar analysis regarding the breakdown of the square-integrability of $\Psi_m$ applies. Thus, as regards the MCHF solution, if the computation is successful it leads to a relatively confined function and to satisfaction of the virial theorem. In fact, convergence becomes generally easier as the nuclear charge is increased even though a number of channels may remain open. When a solution is achieved, the correlating virtual orbital has picked up just a part of the continuous spectrum which does not destroy the square-integrability of the zeroth-order function. In other words, even though the MCHF "$3d$" orbital of the $2s^23d$ configuration represents contributions form the $\epsilon d$ continuous spectrum, it is bound. [This is the common fact for the correlating orbitals in, say, ground-state calculations, for which the singularity of Eq. (10) does not exist.] Of course, the remaining small part of the continuum contributions to the energy from this open channel can be incorporated through the use of Eqs. (3a) and (4), where a complete set of Hartree-Fock scattering orbitals is used.

As an example of such a localization even in a negative ion, consider the three $\text{He}^-$ resonances, $2s2p^{2}\,{}^4P$, $2s2p^{2}\,{}^2D$, and $2p^{3}\,{}^2D^o$. For the $\text{He}^-$ $2s2p^{2}\,{}^4P$ [see Eq. (7)], the average HF radii are $\langle r\rangle_{2s} = 3.96$ a.u., $\langle r\rangle_{2p} = 3.84$ a.u., while for the correlating $3d$ orbital of $2p^23d$, $\langle r\rangle_{3d} = 4.22$ a.u. For $\text{He}^-$ $2s2p^{2}\,{}^2D$, $\langle r\rangle_{2s} = 4.03$ a.u., $\langle r\rangle_{2p} = 4.10$ a.u., and $\langle r\rangle_{3d} = 5.28$ a.u. For $2p^{3}\,{}^2D^o$, the average radii corresponding to the main and to the $(2s2p)^3P^o3d$ correlating configuration are $\langle r\rangle_{2s} = 3.54$ a.u., $\langle r\rangle_{2p} = 4.31$ a.u., and $\langle r\rangle_{3d} = 6.79$ a.u. (and similar magnitudes for $n = 3$ orbitals), in accordance with the expected compactness of these state-specific, self-consistent orbitals.

On the other hand, if for some type of electronic structure it is impossible to obtain valid convergence of the state-specific MCHF equations because of the presence of correlating configurations whose structure corresponds to open channels, then the calculation of $\Psi_0$ excludes them. For example, this is the case of $\text{He}^-$ $2s2p^{2}\,{}^2S$, which interacts with the $2s^2\epsilon s$ continuum. Their effect is then incorporated from principal value integrals over purely scattering function spaces or in terms of suitable $\mathcal{L}^2$ representations of the full continuum. In any case, in the next section we show that at the end of the overall calculation of $E$ and $\Gamma$ of Eqs. (5) and (6b), the results are the same, whether $\Psi_0(\Phi_{\text{MCHF}})$ includes the OCL correlating configurations or not.

## V. CHOICE OF $N$-ELECTRON FUNCTION SPACES FOR $\Psi_0$ AND THE CALCULATION OF $E$ AND $\Gamma$. APPLICATION TO THE $\text{He}^-$ $2p^{3}\,{}^2D^o$ RESONANCE

Arguments [7,8] about the rigorous computation of resonances which are influenced by Feshbach's formalism of resonance formation [27] have pointed to apparent difficulties associated with the presence in our $\Psi_0$ of strongly mixing OCL correlating configurations [28]. For example, in the case of $\text{He}^-$ $2p^{3}\,{}^2D^o$, such a configuration is the MCHF $(2s2p)^3P^o3d$. We have already discussed the physical relevance of such terms in Sec. IV. In this section we study the influence that their presence or absence has on the computation of the observables $E$ and $\Gamma$. We shall show formally and numerically that both $E$ and $\Gamma$ are invariant to the corresponding form of $\Psi_0$, provided the same zeroth-order and virtual orbitals are used. On the other hand, since the OCL configurations contribute dynamically to the radial readjustment of the remaining configurations, a slightly better energy is achieved when the computation includes the OCL configurations in $\Phi_{\text{MCHF}}$.

### A. Case I: Open-channel-like correlating configuration is excluded

Let $\Phi_0$ be a square-integrable configuration-interaction-type wave function representing an $N$-electron resonance, and assume that it excludes the OCL correlating configuration, which we call $\chi^0_{\text{loc}}$. Let $U_\varepsilon$ represent the complete set of scattering states for the open channel. Assume $\langle\Phi_0|U_\varepsilon\rangle = 0$ and let $V_{0E} = \langle\Phi_0|H|U_\varepsilon\rangle$. Then, according to Fano's configuration-interaction theory [29], the exact wave function can be written as

$$\Psi_\varepsilon = (\cos\delta_\varepsilon)U_\varepsilon - \frac{1}{\pi V_{0E}}(\sin\delta_\varepsilon) \times \left[\Phi_0 + \mathrm{P}\int d\varepsilon' U_{\varepsilon'} \frac{1}{\varepsilon-\varepsilon'} V_{0\varepsilon'}\right] , \tag{12}$$

satisfying

$$\langle U_\varepsilon | H-\varepsilon | \Psi_\varepsilon \rangle = 0 \ . \tag{13a}$$

From the condition

$$\langle \Phi_0 | H-\varepsilon | \Psi_\varepsilon \rangle = 0 \ , \tag{13b}$$

it follows that

$$(\cos\delta_\varepsilon) V_{0\varepsilon} - \frac{1}{\pi V_{0\varepsilon}} [\varepsilon - E_0 - \Delta(\varepsilon)] \sin\delta_\varepsilon = 0 \ , \tag{14}$$

i.e.,

$$\tan\delta_\varepsilon = -\frac{\pi V_{0\varepsilon}^2}{\varepsilon - E_0 - \Delta(\varepsilon)} \ , \tag{15}$$

where

$$\Delta(\varepsilon) = \mathrm{P}\int \frac{d\varepsilon' |V_{0\varepsilon'}|^2}{\varepsilon - \varepsilon'} \ , \tag{16}$$

$$\Gamma = \left[ \frac{d\delta}{d\varepsilon} \right]^{-1}_{\varepsilon=E} = \frac{\pi V_{0E}}{1-\Delta'(E)} \tag{17}$$

and $E = E_0 + \Delta$. Now let us see what happens when the square-integrable representation of the open channel, $\chi^0_{\text{loc}}$, is added to $\Phi_0$.

### B. Case II: $\chi^0_{\text{loc}}$ is included

Let

$$\tilde{\Phi}_0 = \frac{1}{\sqrt{1+b^2}} (\Phi_0 + \chi) \ , \quad \langle \tilde{\Phi}_0 | \tilde{\Phi}_0 \rangle = 1 \ , \tag{18}$$

where

$$\chi^0_{\text{loc}} \equiv \chi = \int d\varepsilon' U_{\varepsilon'} S_{\varepsilon'} \ , \quad S_\varepsilon = \langle U_\varepsilon | \chi \rangle \ , \tag{19}$$

and

$$b^2 \equiv \langle \chi | \chi \rangle = \int d\varepsilon' S_{\varepsilon'} \ . \tag{20}$$

Using the same basis set $U_\varepsilon$, we have

$$\langle \tilde{\Phi}_0 | U_\varepsilon \rangle = \frac{S_\varepsilon}{\sqrt{1+b^2}} \ , \tag{21}$$

$$\begin{aligned} W_{0\varepsilon'}(\varepsilon) &\equiv \langle \tilde{\Phi}_0 | H - \varepsilon | U_{\varepsilon'} \rangle \\ &= \frac{1}{\sqrt{1+b^2}} [ V_{0\varepsilon'} + \varepsilon' S_{\varepsilon'} - \varepsilon S_{\varepsilon'} ] \ . \end{aligned} \tag{22}$$

Then

$$\begin{aligned} \Psi_\varepsilon = (\cos\delta_\varepsilon) U_\varepsilon - \frac{1}{\pi W_{0\varepsilon}(\varepsilon)} (\sin\delta_\varepsilon) \\ \times \left[ \tilde{\Phi}_0 + \mathrm{P}\int d\varepsilon' U_{\varepsilon'} \frac{1}{\varepsilon - \varepsilon'} W_{0\varepsilon'}(\varepsilon) \right] \ , \end{aligned} \tag{23}$$

$$\langle U_\varepsilon | H - \varepsilon | \Psi_\varepsilon \rangle = 0$$

by construction, while the condition

$$\langle \tilde{\Phi}_0 | H - \varepsilon | \Psi_\varepsilon \rangle = 0 \tag{24}$$

gives

$$(\cos\delta_{\varepsilon'}) W_{0\varepsilon}(\varepsilon) - \frac{1}{\pi W_{0\varepsilon}(\varepsilon)} (\sin\delta_\varepsilon) [\varepsilon - \tilde{E}_0 - \tilde{\Delta}(\varepsilon)] = 0 \ ,$$

i.e.,

$$\tan\delta_\varepsilon = -\frac{\pi W_{0\varepsilon}^2(\varepsilon)}{\varepsilon - \tilde{E}_0 - \tilde{\Delta}(\varepsilon)} \ , \tag{25}$$

where

$$\tilde{\Delta}(\varepsilon) = \mathrm{P}\int d\varepsilon' \frac{W_{0\varepsilon'}^2(\varepsilon)}{\varepsilon - \varepsilon'} \ . \tag{26}$$

Now, because of (22) we have

$$\begin{aligned} \mathrm{P}\int d\varepsilon' U_{\varepsilon'} \frac{1}{\varepsilon - \varepsilon'} W_{0\varepsilon'}(\varepsilon) = \frac{1}{\sqrt{1+b^2}} \int d\varepsilon' U_{\varepsilon'} \frac{1}{\varepsilon - \varepsilon'} V_{0\varepsilon'} \\ - \frac{\chi}{\sqrt{1+b^2}} \ . \end{aligned} \tag{27}$$

Consider that on the energy shell

$$W_{0\varepsilon}(\varepsilon) = \frac{1}{\sqrt{1+b^2}} V_{0\varepsilon}$$

and referring to the definition of $\tilde{\Phi}_0$, we see that the wave function (23) is identical to the wave function (12). Similarly, it can be shown that

$$\varepsilon - \tilde{E}_0 - \tilde{\Delta}(\varepsilon) = \frac{1}{1+b^2} [\varepsilon - E_0 - \Delta(\varepsilon)] \ . \tag{28}$$

Since $b$ is a constant, the two quantities produce the same $E$, the energy of the resonance. Finally, from (26) it can be shown that

$$1 - \tilde{\Delta}'(\varepsilon) \frac{1}{1+b^2} [1 - \Delta'(\varepsilon)] \ . \tag{29}$$

Thus

$$\Gamma = \left[ \frac{d\delta}{d\varepsilon} \right]^{-1}_{\varepsilon=E} = \frac{\pi W_{0\varepsilon}^2(E)}{1 - \tilde{\Delta}(E)} = \frac{\pi V_{0E}^2}{1 - \Delta'(E)} \ . \tag{30}$$

The above analysis shows that the addition of $\chi^0_{\text{loc}}$ does not change the exact wave function, nor the intrinsic properties $E$ and $\Gamma$ of the corresponding resonance state. The question then is when to include it in $\Psi_0$. We suggest that if a rapid convergence to a reasonably accurate value of the energy is desired without going into the work of computing the interaction with the continuum, then the inclusion in the $\Phi_{\text{MCHF}}$ of OCL bound configurations is advantageous, especially in studies of polyelectronic states. The advantage lies with the physics as well as with efficiency. Thus only a few suitably chosen configurations provide a very good description of the localized part of the resonance, where the interaction with a square-integrable representation of the important open channels is incorporated self-consistently. Contrary to all other methods which use fixed basis sets, this way of including in the overall calculation the effect of bound-continuum interactions allows for the adjustment to the presence of the open channels of the orbitals of the zeroth-order and the major closed-channel configurations.

On the other hand, for multichannel problems, whose rigorous treatment requires the computation of interchannel coupling, if the ICA is to be applied for the calculation of $\gamma_i$ [Eq. (6)], then for reasons of consistency $\Psi_0$ should not include $\chi^0_{\rm loc}$ because this would produce a small but unbalanced contribution of interchannel coupling. For example, if the He$^-$ $2p^3\,{}^2D^o$ $\Psi_0$ contains the $(2s2p)^3P^o3d$ configuration when computing the partial width to the (He $1s2p\ {}^3P^o)\epsilon d$ channel, the interaction of the two terms would slightly distort the assumption of the ICA.

### C. Application to the He$^-$ $2p^3\,{}^2D^o$ resonance

According to the theory in the previous sections, we carried out computations of two types of $\Phi_{\rm MCHF}$ and then of the corresponding $\Psi_0$. Both types of $\Phi_{\rm MCHF}$ included configurations with $n=2$ and $n=3$ orbitals. However, in the first type, called here $\Phi_{\rm MCHF}(1)$, the $(2s2p)^3P^o3d$ configuration is included whereas in the second type, $\Phi_{\rm MCHF}(2)$, it is not. The corresponding eight-term and seven-term MCHF functions and energies, obtained using Froese Fischer's code [30], are given in Table I. Their energies differ considerably: $E_{\rm MCHF}(1)=-0.714\,897$ au.., $E_{\rm MCHF}(2)=-0.695\,861$ a.u., i.e., a difference of 0.518 eV, a number suggesting that the width of this state will also be large, regardless of the size of contributions of other channels. It is noteworthy that the HF energy for He$^-$ $2p^3\,{}^2D^o$ is $-0.660\,813$ a.u., i.e., 61.033 eV above the He ground state. The $E_{\rm MCHF}(1)$ energy is lower by 1.47 eV, corresponding to a position of 59.562 eV above the He ground state.

As regards the scattering states, we computed three sets of $l=2$ scattering orbitals for a large number of energies differing by 0.001 a.u. in the term-dependent HF potentials of the He $2s2p\ {}^3P^o$, $1s2p\ {}^3P^o$, and $1s2p\ {}^1P^o$ states. Such orbitals are expected to be suitable for the reliable calculation of off-diagonal matrix elements [Eqs. (3b) and (6a)], even though their phase shift does not include a small correction due to core polarization.

The choice of the He $1s2p\ {}^{3,1}P^o$ singly excited states as the only other significant thresholds is justified from the following. First of all, consider the case of two-electron emission. The He$^-$ $2p^3\,{}^2D^o$ state, being a MES with empty lower orbitals and high excitation, can also autoionize into the He$^+$ $1s$ continuum, as does the $2s^22p\ {}^2P^o$ state [31,32]. However, given the results of Simons and Kelly [32] on the Li $2s^22p\ {}^2P^o$ state, where the double-electron emission was computed (approximately) to contribute only 7% of the total autoionization rate, we expect that in He$^-$ TES's as well, this decay mode will have a much smaller probability due to near orthogonalities of the orbitals of the main configurations, and therefore we have not considered it.

As regards the He $1snl\ {}^{3,1}L$ channels, their significance or lack of it can be understood from the examination of the coupling matrix elements, $\langle 2p^3|H|1snl\ {}^{3,1}L\epsilon l'\rangle$. Because of symmetry and near-orthogonalities, only the $1s2p\ {}^{3,1}P^o$ terms survive. The very weak coupling of other states, such as He $1s3d\ {}^{3,1}D$, is allowed only via correlating configurations, thereby showing that these states do not constitute important channels for the decay of the He$^-$ $2p^3\,{}^2D^o$ state.

TABLE I. Configurations, their coefficients, and energies of the two MCHF solutions for the compact, zeroth-order representation of the He$^-$ $2p^3\,{}^2D^o$ closed-channel resonance. $\Phi_{\rm MCHF}(1)$ contains the open-channel-like configuration $(2s2p)^3P^o3d$, whereas $\Phi_{\rm MCHF}(2)$ does not. Its large mixing coefficient and the type of interaction matrix element suggest that, by inspection of this compact wave function, it is possible to deduce that the partial width of this state due to the $(2s2p)^3P^o\epsilon d$ channel will be relatively large.

| | $\Phi_{\rm MCHF}(1)$ | $\Phi_{\rm MCHF}(2)$ |
|---|---|---|
| $2p^2$ | 0.859 34 | 0.950 85 |
| $(2s2p)^1P^o3d$ | $-0.101\,15$ | $-0.155\,89$ |
| $(2s2p)^3P^o3d$ | $-0.462\,66$ | |
| $2p(3d^2)^3P$ | $-0.075\,67$ | $-0.084\,67$ |
| $2p(3d^2)^1D$ | 0.036 28 | 0.104 70 |
| $2p(3d^2)^3F$ | $-0.047\,07$ | $-0.031\,28$ |
| $2p(3p^2)^3P$ | $-0.099\,87$ | $-0.124\,31$ |
| $2p(3p^2)^1D$ | 0.134 20 | 0.192 44 |
| | $E(1)=-0.714\,895$ a.u. | $E(2)=-0.695\,861$ a.u. |

The self-consistently correlated core wave function for the He $2s2p\ {}^3P^o$ state is that of Eq. (8). Those of the He $1s2p\ {}^{3,1}P^o$ states were obtained from a nonorthonormal MCHF calculation which allowed for the $2p$ orbitals of the $1s2p$ and $(2p'3d)$ configurations to be different.

$$\begin{aligned}\Phi_{\rm MCHF}({}^3P^o)&=0.9996(1s2p)-0.0207(2s3p)\\&\quad+0.0166(2p'3d)\,,\\E_{\rm MCHF}({}^3P^o)&=-2.1330\ \text{a.u.}\\&\quad(20.972\ \text{eV above the He ground state})\,,\end{aligned}\tag{31}$$

$$\begin{aligned}\Phi_{\rm MCHF}({}^1P^o)&=0.9998(1s2p)+0.0075(2s3p)\\&\quad+0.0206(2p'3d)\,,\\E_{\rm MCHF}({}^1P^o)&=-2.1236\ \text{a.u.}\\&\quad(21.228\ \text{eV above He}\ {}^1S)\,.\end{aligned}\tag{32}$$

This type of computation yields energies which are in very good agreement with the exact energies, $E_{\rm ex}({}^3P^o)=-2.133\,164$ a.u. and $E_{\rm ex}({}^1P^o)=-2.123\,843$ a.u.

Using the above wave functions, the solution of Eqs. (3)–(6) was carried out. The results for the interesting case of the strongly coupled $2s2p\ {}^3P^o\epsilon d$ channel are given in Table II. We see that even though the MCHF wave functions of Table I and their energies are very different, the corresponding energy results of Table II after the inclusion of the continuum are almost the same, the small difference of 0.075 eV being due to the different orbitals of the separately optimized MCHF functions. For $\Phi_{\rm MCHF}(1)$, the energy shift is small and positive whereas for $\Phi_{\rm MCHF}(1)$ it is large and negative. As regards the results on the widths from expressions (5) and (6), the following facts should be noted. The final state did not include core correlation. (This is done for the complete calculation.) There is a small difference between the results

TABLE II. Results for the energy shift and width of the He$^-$ $2p^3\,{}^2D^o$ resonance, for the $2s2p\,{}^3P^o\epsilon d$ channel, using the $\Phi_{\text{MCHF}}(1)$ and $\Phi_{\text{MCHF}}(2)$ of Table I and HF functions for the final states. The large difference between the energy shifts results in a drastic reduction of the deviation of the $E$(MCHF) of Table I, the remaining small difference (0.075 eV) being caused by the slightly different radial functions of the two $\Phi_{\text{MCHF}}$ (see text).

| | Shift (meV) | | Width (meV) | |
|---|---|---|---|---|
| | $\Phi_{\text{MCHF}}(1)$ | $\Phi_{\text{MCHF}}(2)$ | $\Phi_{\text{MCHF}}(1)$ | $\Phi_{\text{MCHF}}(2)$ |
| Eq. (3a) | 40 | −403 | | |
| Eq. (5) | | | 244 | 329 |
| Eq. (6a) | | | 279 | 332 |

from Eqs. (5) and (6) when using $\Phi_{\text{MCHF}}(1)$, i.e., when the OCL configuration is included. The difference between $\Phi_{\text{MCHF}}(1)$ and $\Phi_{\text{MCHF}}(2)$ for Eq. (6a) is due mainly to the different orbitals constituting the two sets of configurations. $\Phi_{\text{MCHF}}(1)$ gave results which are closer to the accurate ones (Table III) with both formulas (5) and (6).

Having obtained $\Phi_{\text{MCHF}}$, we proceeded with the calculation of $\Psi_0$ of Eq. (1), one corresponding to $\Phi_{\text{MCHF}}(1)$, $\Psi_0(1)$, and one corresponding to $\Phi_{\text{MCHF}}(2)$, $\Psi_0(2)$. $X_{\text{loc}}$ contains one-, two-, and three-electron symmetry-adapted correlation functions which are optimized variationally while they are kept orthogonal to the MCHF orbitals as well as to HF orbitals of lower-lying core states.

The electronic structure methods for carrying out such computations have been summarized recently in a brief review of atomic negative ions [25]. First we create symmetry-adapted configurations corresponding to the correlation functions we wish to compute. For the ${}^2D^o$ state the formal subshell expansion of $X_{\text{loc}}$ is

$$X_{\text{loc}}({}^2D^o)=[(2p^2)^3P,{}^1D]\otimes\sigma_{2p}+2p\otimes\pi_{2p^2({}^3P,{}^1D)}+\tau_{2p^3\,{}^2D^o}\ , \tag{33}$$

where $\otimes$ symbolizes the operation of symmetry coupling to form $L^2,S^2$ states.

The correlation functions $\sigma(r_1)$, $\pi(r_1,r_2)$, and $\tau(r_1,r_2,r_3)$ are expanded in terms of spherical harmonics with radial coefficients which are Slater-type orbitals (STO's). In the first step, the radial parts of the pair functions are optimized independently (in the present calculations STO's up to $l=5$ were used), by minimizing the corresponding energy in the presence of the total MCHF function under the orthogonality constraints mentioned above. We then add the configurations containing the $\sigma$ and carry out a configuration-interaction (CI) calculation with $\Phi_{\text{MCHF}}$ and all the terms containing the optimized $\pi$, as well as the $\sigma$ which are now optimized in the presence of $\pi$.

Since the radial optimizations for each pair function are done separately, the $\pi$ (and $\sigma$) are not orthonormal among them. Thus the diagonalization of the full Hamiltonian matrix involves nonorthonormal CI (NONCI) (see [25], and references therein).

The next and final step is the addition of the triple correlation functions $\tau$ and a full NONCI calculation using the complete function of Eq. (33) together with $\Phi_{\text{MCHF}}$. The final results for the two types of $\Psi_0$, $\Psi_0(1)$ and $\Psi_0(2)$ were as follows, for $E_0(1)$ with 98 symmetry-adapted configurations (SAC), and $E_0(2)$ with 97 SAC:

$$E_0(1)|_{98\ \text{SAC}}=-0.719\,114\,4\ \text{a.u.}=59.447\ \text{eV}\ , \tag{34a}$$

$$E_0(2)|_{97\ \text{SAC}}=-0.701\,566\,3\ \text{a.u.}=59.924\ \text{eV}\ . \tag{34b}$$

Finally, using the $\Psi_0$'s we computed again Eqs. (3)–(6), this time including core correlation in the final state [Eqs. (8), (31), and (32)]. The total energies are [Eq. (4)]

$$E(1)=-0.718\,688\,0\ \text{a.u.}=59.458\ \text{eV}\ , \tag{35a}$$

$$E(2)=-0.713\,215\,9\ \text{a.u.}=59.607\ \text{eV}\ , \tag{35b}$$

and the total width [Eq. (6)] is

$$\Gamma(2)=282\ \text{meV}\ . \tag{36}$$

The breakdown of these numbers is given in Table III. The total energy $E(1)$ and the width $\Gamma(2)$ are the ones adopted for reasons which were discussed earlier. We note that for the important $2s2p\,{}^3P^o\epsilon d$ channel, the two wave functions $\Psi_0(1)$ and $\Psi_0(2)$ gave the same partial widths with the exact formula (6): $\gamma(1)=253$ meV, $\gamma(2)=252$ meV. As already explained, the difference of 0.161 eV between $E(1)$ and $E(2)$ is due mainly to the relaxation of the MCHF orbitals in the presence of the OCL configuration and to the related adjustment of the optimized virtual orbitals entering in $X_{\text{loc}}$. From $E_0(1)$ of (34a) and the HF energy of $-0.660\,813$ a.u., it follows that the localized correlation energy in this case is 1.575 eV, of which 1.471 eV (93%) is picked up just by the $\Phi_{\text{MCHF}}(1)$ of Table I.

Finally, given the interest in relating the autoionizing states to the nearby thresholds and in characterizing them as closed-channel (Feshbach) or open-channel (shape) resonances, we note that the He$^-$ $2p^3\,{}^2D^o$ state can be called "Feshbach" with respect to the He $2p^2\,{}^1D$

TABLE III. Final results for the energy shift and width for the He$^-$ $2p^3\,{}^2D^o$ resonance using $\Psi_0(1)$ and $\Psi_0(2)$ (see text) and correlated (uncorrelated) core [Eq. (8)] with HF scattering orbitals for the important $2s2p\,{}^3P^o\epsilon d$ channel. As regards the other two channels, $1s2p\,{}^{3,1}P^o$, only the $\Psi_0(2)$ wave function was used for reasons of consistency (see text). It gave $\delta(1s2p\,{}^3P^o)=10$ meV, $\gamma(1s2p\,{}^3P^o)=21$ meV, $\delta(1s2p\,{}^1P^o)=2$ meV, $\gamma(1s2p\,{}^1P^o)=9$ meV. In this case, neither core correlation nor the use of Eq. (5) (golden rule) made any difference. For $\Psi_0(1)$, the energy shift of the $2s2p\,{}^3P^o\epsilon d$ channel is very small (12 meV) because it has already been included in the overall variational calculation through the MCHF OCL configuration. As a final total energy we adapted the slightly lower $E(1)$ (see text), which corresponds to 59.46 eV above the He ground state.

| | Shift (meV) | | Width (meV) | |
|---|---|---|---|---|
| | $\Psi_0(1)$ | $\Psi_0(2)$ | $\Psi_0(1)$ | $\Psi_0(2)$ |
| Eq. (3a) | 12 | −317 | | |
| Eq. (5) | | | 230 | 286 |
| Eq. (6a) | | | 253(256) | 252(276) |

autoionizing state at 59.91 eV [27] or with respect to the He $2p^2\,{}^3P$ discrete state at 59.68 eV [33].

## VI. THE He$^-$ $2s2p^2\,{}^2P$ STATE: IS IT A SHAPE OR A FESHBACH RESONANCE?

Since the beginning of the application of scattering-type formalisms, such as that of Feshbach or of close-coupling theory (see, e.g., [27,34]), to the computation of resonances in atoms and molecules, the notions of closed-channel (or Feshbach) and open-channel (or shape) resonances have been widely used. In fact, they have occasionally been elevated to the level of an important issue, as, for example, with the case of the doubly excited He$^-$ $1s2s2p\,{}^2P^o$ resonance [8,27,35,36] or of the triply excited $2s2p^2\,{}^2D$ resonance [7,8]. This emphasis has its roots in the fact that these methods examine the system "electron plus target." As Burke (Ref. [34], p. 174) summarizes, "Closed channel resonances arise when the interaction potential between the incident particle and an excited state of the target is strong enough to support a bound state. They lie energetically below the channel or channels to which they are most strongly coupled, while shape resonances lie energetically above."

As already stressed, they present state-specific theory does not involve a "target" state and corresponding concepts or computational constraints. Instead, it aims directly for the wave function of the localized component of the decaying state which is characterized by its own electronic structure-dependent multiconfigurational self-consistent field. This approach renders the question of Feshbach vs shape resonance without computational or physical significance. Consideration of a nearby threshold enters only for establishing whether it contributes to the width or not. On the other hand, if the desire exists, it is still possible to understand the character of the state under examination by analyzing the major configurations in conjunction with the energy results. For example, for the aforementioned He$^-$ $1s2s2p\,{}^2P^o$ resonance. Komninos, Aspromallis, and Nicolaides [19] demonstrated that just a two-term, properly coupled MCHF wave function predicts that this state is mainly Feshbach in nature, although "it contains smaller parts than can be expanded in terms of the wave functions of the open channels $1s2s\,{}^2S\epsilon p$ and $1s^2\epsilon p$." In harmony with the analysis of this work, they added (Ref. [19], p. 1867), "So, we have absorbed part of the open channels into the localized part $\Phi$ of the resonance and, in doing so, we included part of the energy shift $\Delta$ into $E_0$."

The He$^-$ $2s2p^2\,{}^2P$ state studied here constitutes another prototypical case where the Feshbach-vs-shape question can be asked. This is because, when seen from a scattering point of view, there are three physically relevant doubly excited thresholds which may be thought of as parent states: He $2s2p\,{}^3P^o$ ($E=58.31$ eV), $2p^2\,{}^3P$ ($E=5.68$ eV), and $2s2p\,{}^1P^o$ ($E=60.15$ eV). The computations described below included configurations representing the coupling of these channels, as well as of many others.

First, an 11-term $\Phi_{\mathrm{MCHF}}$ (Table IV) was calculated as the self-consistent representation of the localized part of the He$^-$ $2s2p^2\,{}^2P$ state. Using these $2s$ and $2p$ orbitals, the single configuration energy $E(\mathrm{HF})=-0.660\,550$ a.u. $=61.040$ eV above He. The MCHF energy is $E(\mathrm{MCHF})=-0.706\,994$ a.u. $=59.776$ eV above He, producing an electron correlation lowering of 1.264 eV. These two results immediately establish that the He$^-$ $2s2p^2\,{}^2P$ resonance is between the He $2s2p\,{}^1P^o$ and $2s2p\,{}^3P^o$ thresholds but leaves open the question as to its position with respect to the He $2p^2\,{}^3P$ state.

TABLE IV. Configurations, their coefficients, and the energy of the MCHF solution for the compact, zeroth-order representation of the He$^-$ $2s2p^2\,{}^2P$ valence shape resonance. The $4d$ orbital was included in the Fermi-Sea because it was found that it helped convergence. The most significant mixing comes from the $2s\rightarrow 3d$ orbital excitation, a correlation effect having the physical significance mediating of the coupling to the He $2s2p\,{}^3P^o$ and ${}^1D$ thresholds. Note that the combination $(2s2p^2+2s3p^2)$ includes, via orbital rotation, the contribution of $2s2p3p$, whose structure is the same as that of the open channel $(2s2p)^3P^o\epsilon p$.

| | |
|---|---|
| $2s2p^2$ | 0.9150 |
| $2s3p^2$ | −0.0869 |
| $3d(2p^2)^3P$ | 0.2101 |
| $3d(2p^2)^1D$ | −0.2783 |
| $(2p3s)^1P^o3p$ | 0.1239 |
| $(2p3s)^3P^o3p$ | −0.1229 |
| $2s4d^2$ | −0.0357 |
| $2p(3p4d)^1P^o$ | 0.0084 |
| $2p(3p4d)^3P^o$ | 0.0239 |
| $2p(3p4d)^1D^o$ | −0.0102 |
| $2p(3p4d)^3D^o$ | 0.0351 |

$E=-0.706\,993\,8$ a.u.

The MCHF energy contains to a large part the contribution from the $2s2p\,{}^3P^o\epsilon p$ open channel through the MCHF mixing $2s(2p^2+3p^2)$, which eliminates the OCL configuration $2s2p3p$. Also, the contribution from the $2p^2\,{}^3P\epsilon d\,{}^2P$ channel, which at this stage of the computation might appear to be open, is included through the configuration $(2p^2)^3P3d$. Furthermore, Table IV reveals that the $2p^2\,{}^1D$ channel (the corresponding He state is at 59.91 eV [27]) also couples strongly, even though the usual qualitative arguments of orbital structure and symmetry would exclude it as a parent state for He$^-$ $2s2p^2\,{}^2P$. Stated in a different way, the closed-channel relation of the He$^-$ $2s2p^2\,{}^2P$ resonance to the He $2p^2\,{}^2D$ threshold is revealed only when electron correlation is considered.

Carrying out the computation as in Sec. V, the following energy results were obtained:

$$E_0|_{95\ \mathrm{SAC}}=-0.710\,934\ \text{a.u.}=59.669\ \text{eV}\ , \tag{37a}$$

$$\Delta=0.001\,36\ \text{a.u.}=37\ \text{meV}\ , \tag{37b}$$

$$E=E_0+\Delta=-0.709\,570\ \text{a.u.}=59.706\ \text{eV}\ . \tag{37c}$$

These results once again reveal the benefits of computing MES's in terms of state-specific, selected few MCHF configurations. For example, the energy difference between the 11-term $\Phi_{\mathrm{MCHF}}$ and the 95-term $\Psi_0$, including the energy shift, is only 0.070 eV.

The energy results, in combination with the characteristics of $\Psi_0$, show the following. The He$^-$ $2s2p^2\,{}^2P$

state contains components which correspond to coupling to four nearby thresholds, the He $2s2p\ ^3P^o$, $2p^2\ ^3P$, $2p^2\ ^1D$, and $2s2p\ ^3P^o$ (see Table IV). It is a shape resonance with respect to the $2s2p\ ^3P^o$ state to which it is connected by a single orbital excitation. The interaction between the localized and continuum components is possible even in zeroth order, since the HF orbitals in initial ($2s2p^2$) and final [$(2s2p)^3P\epsilon d$] configurations are not orthonormal. Of course, when correlation is included, additional energy and overlap matrix elements contribute [see Eqs. (3)–(6)].

At the same time, the He$^-$ $^2P$ resonance is clearly below the He $2p^2\ ^1D$ and $2s2p\ ^1P^o$ thresholds—while our computed energy places it only 0.025 eV above the He $2p^2\ ^3P$ state. However, we expect that this small difference is covered by the remaining localized correlation which pushes the He$^-$ resonance just below the He $2p^2\ ^3P$ threshold, rendering it a Feshbach resonance with respect to this threshold as well, which it also overlaps via its finite width of $\Gamma = 79$ meV [Eq. (38)].

Having chosen the open channels according to all the previous arguments as the He $2s2p\ ^3P^o$, $1s2p\ ^1P^o$, and $1s2p\ ^3P^o$, the final computations of the width were carried out. The partial shift for the $2s2p\ ^3P^o\epsilon p$ channel is 35 meV, and the partial width is 60 meV. Also, $\gamma(1s2p\ ^3P^o) = 9$ meV and $\gamma(1s2p\ ^1P^o) = 10$ meV. Thus the total width is

$$\Gamma = 79 \text{ meV} . \tag{38}$$

## VII. CONCLUSION

We have discussed how polyelectronic autoionizing states can be computed within the framework of state-specific theory, regardless of whether they are doubly, triply, quadruply, etc., excited, regardless of their symmetry, and regardless of the relative position of corresponding thresholds. Emphasis was given on the justification and efficiency of starting the overall computation with a suitably chosen set of self-consistently optimized configurations. Formal and numerical results were presented regarding the calculation of the width and the type of correlating configurations which enter $\Psi_0$, the wave function of the localized part of the resonance. It was shown that if open-channel-like bound configurations are included in the MCHF solution, efficient convergence to an energy which is close to the exact one is achieved, since much of the bound-continuum interaction is included self-consistently. As an application, the existence of two new $n=2$ intrashell triply excited resonances of He$^-$, the $2p^3\ ^2D^o$ ($E = 59.46$ eV, $\Gamma = 282$ meV) and the $2s2p^2\ ^2P$ ($E = 59.71$ eV, $\Gamma = 79$ meV) has been predicted. Given the structure of the three open thresholds involved and the related very small coupling due to the required $1s \rightarrow 2s$ excitation, the widths were obtained by applying Eq. (6) and the independent channel approximation, i.e., by omitting interchannel coupling. The resulting error ought to be insignificant. Our partial-width computations show that both resonances decay primarily to the He $2s2p\ ^3P^o$ threshold, which itself is autoionizing, but with a longer lifetime ($\Gamma = 0.009$ eV).

Finally, in conjunction with earlier experimental and theoretical results, the present findings show that the recently measured [1] new structures at $58.415 \pm 0.005$ and $58.48 \pm 0.02$ eV cannot correspond to the He$^-$ $2p^3\ ^4S^o$ and $^2D^o$ states, nor to any other He$^-$ $n=2$ intrashell state. New experiments for the region 58–60 eV ought to allow verification of the above predictions and conclusions.

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