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State-specific approach and computation of resonance states: Identification and properties of the lowest $^2P^o$ and ^2D triply excited states of He$^-$

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We discuss aspects of the theory and computation of resonance (autoionizing) states of polyelectronic atoms and their positive and negative ions, in the context of the state-specific approach, using as paradigms the He$^-2s^22p\ ^2P^o$ and $2s2p^2\ ^2D$ triply excited states. The He$^-\ ^2D$ resonance has been the subject of controversy about its nature and its very existence, with ramifications as to the physics of electron-He scattering measurements and as to the theory of resonance states in multiparticle systems in general. By carrying out a series of computations, we show how (quasi)localization of these resonances takes place. The results confirm the existence of the ^2D resonance just below the energy of the He $2s2p\ ^3P^o$ resonance, with which it overlaps. The localization of the two He$^-$ resonances is achieved already at the single-configuration level, provided the orbitals are calculated by solving state-specific restricted Hartree-Fock (HF) equations. Accounting for orbital flexibility and relaxation due to the self-consistent interactions is essential to the achievement of a local energy minimum. The localized nature of the wavepacket is revealed even more definitely by solving appropriate multiconfigurational HF (MCHF) equations containing the information from the self-consistent interaction with closed channels as well as with the neighboring significant open ones. Reaching a reliable MCHF solution for a variety of polyelectronic multiply excited states may often be difficult, but once it is achieved it provides the overwhelmingly dominant characteristics of the state. It is then used as the reference wave function for computing variationally the remaining of the localized electron correlation in terms of optimized analytic orbitals representing very nearly the full space of the electron virtual excitations. The calculation of the localized part Ψ_0 and of $E_0=\langle\Psi_0/H/\Psi_0\rangle$, is done by nonorthonormal configuration interaction (NONCI) since parts of Ψ_0 are optimized separately in terms of their own basis sets. The final $\Psi_0 s$ for the two resonances consisted of 683 symmetry-adapted configurations for the $^2P^o$ state and 778 ones for the ^2D state. Using these functions and final state scattering functions with continuum orbitals obtained numerically in term-dependent core potentials, without and with polarization, of a number of lower-lying open channels, we employed the independent channel approximation and computed partial and total energy shifts and widths, the latter from energy-dependent golden rule expressions. Critical comparison of our results for $E=E_0+\Delta$, where Δ is the shift induced by the interaction of Ψ_0 with the continuum, and for the width, Γ, with the existing few experimental and theoretical values, led us to the conclusion that the E and Γ lie in the following ranges: For the $^2P^o$ state: $E=57.204\pm0.005$ eV, $\Gamma=68-74$ meV, and for the ^2D state: $E=58.295\pm0.010$ eV, $\Gamma=38-55$ meV. Of special theoretical and experimental interest is the determination of the partial and total widths of the three-electron He$^-\ ^2D$ resonance, since it overlaps from below the two-electron threshold state He $2s2p\ ^3P^o$, whose position is at 58.312 eV with a width of 8 meV.

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I. INTRODUCTION

Coulomb interactions in He$^-$ give rise to resonances in the continuous spectrum, which in the approximation of the single-configuration assignment, can be classified into doubly excited states (DES) and triply excited states (TES). Similar excitations can occur in larger atoms as well. It is then reasonable to assume that DES and TES of He$^-$ contain prototypical features for the testing of theory and of computational methods aiming at the quantitative understanding of the formation, of the electronic structure and of the intrinsic properties of such states in general. Furthermore, the He$^-$ system is attractive from the point of view of theory, since its small number of electrons offers the possibility of reliable calculation taking into account the interactions of all the electrons.

The theory of resonance formation and calculation that is discussed in this paper and that has been given the generic name of *state-specific approach* (SSA), provides the recipe for dealing with DES and TES of He$^-$ as well as of larger atoms. The present work continues the research program of exploring the properties of prototypical resonance states of arbitrary structures and the efficiency of methods of the SSA (Refs. [1,2], and references therein). It was instigated by the contents of the review of Buckman and Clark [3] and of four regular papers, three experimental [4–6] and one theoretical [7], which left open questions about the physics and the theory of He$^-$ resonances. The resolution of the problems created by the measurements of [4–6] is presented and discussed in Ref. [8]. Here we are mainly concerned with the foundations and the methods of the theory, the presentation

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of new results on the properties of the two He^- resonances, and with the issues raised by Chung [7], who discusses the formation and the existence or nonexistence of resonances, with exemplars from TES of He^- and H^{2-}. In particular, Chung [7] rejects the possibility of formation of $2s2p^2\ {}^2D$ resonance in He^- as well as that of a $2p^3\ {}^4S^o$ resonance in H^{2-}, contrary to other theory and results for He^- [1,2,9] and for He^{2-} [10,11], which support the existence of these resonances.

Although the analysis and comparisons that will be presented in the following sections concern the two He^- TES, the conceptual and computational framework of the present study transcends the particular multiply excited resonances and is relevant to the field of resonance states in multielectron atoms in general.

The structure of the paper is as follows: In Sec. II we present the background of the controversy and apparent uncertainty surrounding the identification and calculation of the $\mathrm{He}^-\ 2s2p^2\ {}^2D$ state, an issue which we hope that the present work resolves conclusively. In Sec. III we stress upon the significance of an integral part of the SSA, namely, the calculation and use of properly chosen state-specific multiconfigurational Hartree-Fock (MCHF) solutions as zero-order reference wave functions. We cite as examples earlier results whose essence as regards accuracy and the capacity to relate electronic structure to resonance formation and decay is relevant to the present discussion. In Sec. IV we review briefly the method of calculation of the energy shift and width. In Sec. V we present our analysis and a series of results on the $2s^22p\ {}^2P^o$ and $2s2p^2\ {}^2D$ He^- triply excited resonances obtained from the application of notions and methods of the SSA. Their reality is assured by the fact that there indeed exists a localized wavepacket, which is computed both with small expansions with self-consistent orbitals as well as with completely correlated wave functions Ψ_0. Using these Ψ_0 and scattering functions for each of the major open channels, where the scattering orbital is calculated in the potential of single or MCHF cores with exchange, we computed E, Γ, and the partial widths. In all energy conversions we used $E(\mathrm{He}\,{}^1S) = -2.903\,724$ a.u. and 1 a.u.(He) = 27.207 7 eV $= 27.211\,396 \times (1 - m_o/M_{\mathrm{He}})$.

II. THE PARADIGM OF THE $\mathrm{He}^- 2s2p^2\ {}^2D$ RESONANCE

It is rather straightforward to understand the appearance and the properties of a resonance state whenever a single-particle description is applicable. This is usually presented in textbooks in terms of a volcanolike potential, with a local energy minimum and a barrier through which the particle tunnels. However, for polyelectronic states such as the TES of He^-, the comprehension of their formation and of their properties must engage not only the formal aspects of the quantum mechanics of resonance states but also proper analysis and computational methods for the treatment of excited electronic structures with strong electron correlation.

The literature on resonances in the electronic spectra of atoms and molecules suggests that the $\mathrm{He}^-\ 2s2p^2\ {}^2D$ state may be considered as a paradigm for the field, where crucial elements of theory, of measurement techniques and of interpretation have been tested. The review that follows provides the background that is essential to the arguments and results of the present paper.

Following the appearance of structures in the measurements of the $\mathrm{He}+e^-$ collision cross-section at energies 57–60 eV by Kuyatt, Simpson, and Mielczarek [12], Fano and Cooper [13] conjectured, without calculation, that these should be interpreted as He^- resonances with the assignment of $n=2$ intrashell configurations. In particular, for the structure at 58.3 eV, Fano and Cooper proposed, with some reservation, the assignment of $2s2p^2\ {}^2D$. A few years later, the first *ab initio* calculations on TES of He^- by Eliezer and Pan [14] and by Nicolaides [1(a)] found square integrable solutions, via different methods, with energies around 58.3–58.4 eV and with the $2s2p^2\ {}^2D$ configuration as the main component.

However, objections and doubts as to the identification of this structure with the $2s2p^2\ {}^2D$ resonance state were published by Chung [15] and by Chung and Davis [16]. Based on their model, which is discussed in the following sections, they obtained the total energy of the He^- state as a function of a nonlinear parameter of analytic orbitals representing the projectile electron that is coupled to fixed two-electron wave functions representing various target states. From the repulsive form of the interaction that was seen when the He $2s2p\ {}^3P^o$ target wave function was considered, a type of computation that is further discussed in Ref. [7], they concluded that no $2s2p^2\ {}^2D$ resonance can be formed. Thus, in their 1985 paper Chung and Davis [16] stated: “This result does not corroborate the previous assignment by Fano and Cooper. What has been seen in the experiment could be the result of a postcollision interaction effect.” These conclusions were registered by experimentalists (e.g., [5,17]) who, in their discussion on the origin of structures in their scattering data, referred to the supposed lack of conclusive theoretical support for the existence of the ${}^2D$ resonance. For example, in 1991, Batelaan, van Eck, and Heideman [17] wrote: “The identification of the 58.3 eV resonance is still not completely clear” (p. 5152)...“Theoretically the identification of the 58.3 eV resonance still does not seem to be resolved. The theoretical result of Chung (1980) shows that a He $(2s2p)^3P^o$ core is repulsive to a $2p$ electron when a resonance is searched variationally.”

The discussions in Refs. [7,15–17] contradict our theoretical predictions and analysis [1,2,9], and a number of experimental measurements and interpretations as to the existence of this triply excited He^- resonance [4–6,12,17–21]. In an exchange of views on the background of the theory and methods of calculation of resonances [1(c),22], it was stated [[1(c)] p. 693] that “*this resonance is real, regardless of whether it is above or below the* He $2s2p\ {}^3P^o$ *threshold*.” Detailed analysis as to the fundamental importance of localization and as to the contribution of the *open-channel-like* (OCL) bound configurations with self-consistent orbitals was presented in Refs. [1,2]. In our work, the self-consistently computed OCL configurations constitute part of the zero-order reference space and, in cases of multiply excited states with closely lying thresholds, are indispensable to the economy of a well-converged state-specific calculation.

Finally, large-scale complex-coordinate-rotation (CCR) calculations with mixed orbital and r_{12} basis sets were undertaken by Bylicki and Nicolaides [9], which clearly identified the corresponding complex eigenvalue, with an eigenfunction consisting mainly of *spp*, *ssd*, *dpp*, and *spf* components. (In the SSA context, these are represented mainly by configurations $2s2p^2$, $2s2pp$, $2s^2d$, $2p^2d$, $2ppd$, and $2s2pf$—see Sec. V.) In fact, its energy was found to be slightly below the He $2s2p\ ^3P^o$ threshold at -0.76052 a.u. in agreement with the measurement of Gosselin and Marmet [6] and in conceptual and computational disagreement with the theory of Chung. Specifically, the energy of the ^2D state was found to lie 10 meV below that of the He $2s2p\ ^3P^o$ state, but the states overlap due to the calculated width of 49 meV. The energy for the $2s^22p\ ^2P^o$ resonance was computed to be at 57.205 eV above the He ground state, and that of the ^2D resonance at 58.303 eV. The experimental values of Hicks *et al.* [18] are 57.22 ± 0.04 and 58.30 ± 0.04 eV and of Roy, Delage, and Carette [19] are 57.19 ± 0.03 and 58.29 ± 0.03 eV, respectively. Even more accurately has been measured the energy difference between the two He^- resonances [19], which gave $\Delta E=1.094\pm0.012$ eV. This number agrees excellently with the theoretical value [9] of 1.098 eV. The width of the ^2D resonance has been measured as 50 ± 20 meV by Quemener, Paquet and Marmet [20], as 59 ± 4 meV by Gosselin and Marmet [6], and as 40 ± 10 meV by van den Brink (quoted in Ref. [17]).

With his recent paper, Chung [7] has returned to his earlier arguments, with results and conclusions aiming at the comprehension of the formation of multiparticle resonances. Following the results of calculations that focus on obtaining a local energy minimum through the hierarchical mixing of correlated wave functions $2p^2\ {}^1D\varphi(s)$, $2s2p\ {}^1P^o\varphi(p)$, $2p^2\,({}^3P,{}^1D,{}^1S)\varphi(d)$, $2s2p\ {}^3P^o\varphi(p)$, and the variational optimization of the orbitals $\varphi(1)$, (variation of one nonlinear parameter), he concluded that the ^2D state is not associated with an attractive potential. He states (p. 2784 of Ref. [7]). "*In an earlier work it is pointed out that the ^2D structure cannot be a Feshbach resonance. The results in this study appear to reaffirm this conclusion.*" [We add: If the repulsive curve presented in Ref. [7] represented a physical situation, (it does not), then the extra electron could not bind as a shape resonance either.]

In view of the above, and especially of the recent paper [7], we thought that additional exploration of this question would provide timely and valuable insight into the nature of this resonance state as well as into the theory of resonance formation in multielectron atoms and molecules in general. To do this, we carried out a variety of both small- and large-scale SSA calculations and have made comparisons with results and conclusions of Refs. [7,15,16]. In the following sections we will show that these conclusions result substantially from the structure of the approach of Refs. [7,15,16] and from an inadequate implementation of the conceptual framework "$(N\text{-}1)$-*electron target plus extra electron.*" One of the consequences is that the results and conclusions of Refs. [7,15,16] about the prototypical $\mathrm{He}^-\ {}^2D$ resonance must be corrected.

III. APPLICABILITY AND UTILITY OF STATE-SPECIFIC ZERO-ORDER MULTICONFIGURATIONAL WAVE FUNCTIONS OBTAINED SELF-CONSISTENTLY

The emphasis of the SSA is on the recognition of the significance of Ψ_0 and on its reliable calculation via techniques that were initially developed for the computation of electronic structures of ground or low-lying discrete states. In the paper where the foundations of the SSA were laid [1(a)], (in [1(a)] there are a few typographical errors), the zero-order approximation to Ψ_0 was computed self-consistently at the term-dependent single-configuration level by implementing the Roothaan analytic HF method [23], where each orbital *nl* is expanded in a small set of Slater functions with nonlinear parameters that are determined during the self-consistent procedure optimizing the HF solution. At that time, no analytic or numerical HF theory had been successfully applied to the calculation of zero-order approximations to such multiply excited resonances of atomic negative ions (ANIs). Apart from practical questions regarding the reliable convergence of calculations for such states, there was also the question of the validity of applying HF theory to states in the continuous spectrum where the energy-minimum principle does not hold. It was argued [1,2] that the shell structure and orbital variational constraints, together with the satisfaction of the virial theorem and of the physically meaningful behavior of the occupied orbitals and of the interaction integrals, constitute valid wavepacket localization criteria, which in conjunction with computational experience, are sufficient for the direct calculation of zero order and correlation contributions to Ψ_0 and E_0. The accuracy of the analytic HF solutions was verified a few years later, when the numerical HF method was implemented, following the availability of Froese-Fischer's program in the mid 1970s [24]. For example, the analytic HF energy for He^- $2s2p^2\ {}^2D$ obtained in Ref. [1a] using five Slater-type orbitals (STOs) of *s* symmetry and four STOs of *p* symmetry is -0.70747 a.u. The numerical HF energy is -0.70772 a.u. if the $2s$ orbital is not kept orthogonal to the He^+ $1s$ and $-0.708\,09$ a.u. if it is kept orthogonal. These HF energies place the $\mathrm{He}^-\ {}^2D$ position at 59.4–59.5 eV above the ground state. As we recommend is this paper (Sec. V), the accurate value is 58.295 ± 0.010 eV.

For the open shell structures of excited states, obtaining a self-consistent HF solution constitutes a serious computational advantage over the use of fixed basis sets, since the orbitals are term-dependent to a significant degree. Nevertheless, the single configuration representation is, in general, not a good zero-order approximation for the highly correlated DES and TES. Furthermore, because of strong mixings and of the presence of lower states of the same symmetry, it may not be possible to obtain a reliable solution. On the other hand, experience from solving numerically the MCHF equations for excited states has revealed that starting the overall calculation of resonance states based on MCHF zero-order approximations Φ_0^k with appropriately chosen configurations, constitutes a very efficient and accurate approach to the problem of computing properties of such states. Thus, for each state $|k\rangle$, the localized part Ψ_0^k is computed in the form

$$\Psi_0^k = a\Phi_0^k + bX_{\mathrm{loc}}^k, \quad a^2+b^2=1, \tag{1}$$

where a^2 is overwhelmingly dominant, with $a\Phi_0^k$ remaining compact and representing the principal features of Ψ_0^k.

In general, both parts Ψ_0^k and X_{loc}^k contain all the terms of the function space contributing to the localization of $|k\rangle$. The radials and the coefficients of the few critical configurations in Φ_0^k produce an optimal description, a fact that minimizes the importance of X_{loc}^k and the extra work needed for its calculation. The correlation orbitals entering into X_{loc}^k are optimized separately while being kept orthogonal to those of Φ_0^k as well as to those of subshells of lower states of the same symmetry. The separate variational optimization of the term-dependent one-, two-, three-, etc. electron-correlation functions in X_{loc}^k improves convergence but, in general, also requires the use of nonorthonormal orbitals.

A. Techniques for achieving convergence of self-consistent calculations of resonance states of polyelectronic atoms

As expected, localization, and hence the calculation of Ψ_0^k, occurs much more readily in the neutrals and positively charged autoionizing states than in the resonance states of the ANIs. This implies that properties of inner-hole Auger states or multiply excited states (MES) of positive ions, can be predicted by economic MCHF calculations, if most of the significant correlation effects are included [2(b)].

On the other hand, because of the weak binding that the ANI resonances have in general, it is often very difficult, or even impossible, to solve the HF or the MCHF equations, since one of the orbitals becomes, during the iteration, extremely diffuse, tending to a scattering orbital while the energy is lowered, unphysically, to the corresponding fragmentation threshold. For example, we refer to a fact on which we commented in p. 3582 of Ref. [2(a)] and p. 4145 of Ref. [2(b)]: Whereas it is rather straightforward to obtain an MCHF solution of the $2s2p^2\ ^2S$ TES for Li and the isoelectronic positive ions, it is impossible to do so in He$^-$ if the $2s^2s$ configuration is included, since the s function cannot be made to bind when the self-consistent-field results (SCF) iteration is allowed freely.

As we already mentioned, during the first stages of the implementation of the SSA to MES and to inner-hole states, the zero-order reference wave function was a single configuration with HF orbitals. If one starts with a HF wave function, consideration of interelectronic interactions leads to correlation configurations representing the adjacent continuous spectrum, i.e., open channels. Using as simple examples configurations such as $1s^2 2p^2\ ^1S$ and $1s2s^2\ ^2S$, it was discussed in p. 2088 of Ref. [1(a)] and p. 462 of Ref. [1(b)] how the contribution of *hole-filling* pair correlations can be computed approximately using judiciously chosen configurations with bound orbitals. Of course, better and rigorous approaches, free from uncertainties and inaccuracies regarding the representation of the continuum, are attained by using numerically calculated Rydberg bound and free scattering orbitals for each channel, [2,25–27], or optimized complex L^2 orbitals [28–30].

When it was later found that the solution of the state-specific MCHF equations for properly selected configurations can be achieved numerically by using Froese-Fischer's computer program [24], we started implementing resonance scattering theory using the form (1) [e.g., [26(b)]]. It is then possible to account for part of the contribution of the discrete-continuum interactions self-consistently, by including in Φ_0^k OCL configurations [2]. However, obtaining reliable solutions of the resulting MCHF equations is far from simple in many cases. In order to achieve such solutions, we have developed a few techniques which are crucial where failure appears to be the normal result. These take into account properties of the electronic structure of the state of interest and the related form of the HF and MCHF equations. Needless to add, it is understood that the numerical aspects of integration of the coupled differential equations must be as accurate as possible.

One such technique is suitable for electronic structures whose energy is found above their own threshold. The first application was reported by Beck and Nicolaides [11(a)], when they dealt with the calculation of the shape resonance $2p^3\ ^4S^o$ of the H^{2-} doubly negative ion. A similar calculation was reported recently in Ref. [25] on the Li$^-$ $1s^2 2s2p\ ^3P^o$ shape resonance. The technique has been used in a few more cases. It involves the iterative combination of SCF and single excitation configuration interaction (CI) procedures, whereby the orbital expansion in the CI is collapsed into an orbital of the same symmetry, which is then used in the SCF equations in order to obtain a bound SCF orbital for the loosely attached electron. The reader is referred to Refs. [25,11(a)] for details.

Another technique, which was used in the present calculations of the He$^-$ $2s2p^2\ ^2D$ resonance state, involves the handling of certain OCL configurations that are deemed important for the accurate description and proper convergence of the MCHF Φ_0^k. It was first used in order to achieve a simple and physically transparent MCHF solution for the He$^-$ $1s2s2p\ ^2P^o$ broad resonance and to recognize the fact that this state has components of both *Feshbach* and *shape* resonances [26(b)]. This technique aims at making worthy the possible advantages that different orbital couplings may have, as well as at obtaining a better physical picture. Specifically, let us look at the He$^-$ $2s2p^2\ ^2D$ resonance. Three types of orbital replacement lead to OCL configurations (i), (ii), and (iii) below, since both the He $2s^2\ ^1S$ and He $2s2p\ ^3P^o$ thresholds are open when an approximate calculation on the He$^-$ $2s2p^2\ ^2D$ state is done. (When all interactions, including those of the continuum are accounted for, the He$^-$ ^2D energy is found below the He $2s2p\ ^3P^o$ energy).

$$\psi(2s2p^2)\ ^2D \leftrightarrow \mathrm{He}\ \psi(2s^2\ ^1S)d$$

(i) (hole-filling pair correlation)

(ii) $\leftrightarrow \mathrm{He}\ \psi(2s2p\ ^3P^o)p$

(iii) $\leftrightarrow \mathrm{He}\ \psi(2s2p\ ^3P^o)f.$

The orbitals p, d, and f need not be hydrogenlike $3p$, $3d$ or $4f$. All three configurations (i), (ii), and (iii), represent interactions that contribute to both resonance formation and to its energy. As we will argue in Sec. V and as we have discussed before [2], the inclusion of configuration (i) into a large MCHF calculation causes no convergence problems, while contributing significantly to the character of Ψ_0. The same holds for configuration (iii), albeit with a smaller contribution. However, when configuration (ii) is included in an MCHF calculation with either a small or a large expansion, the solution fails since the outer $\overline{p}$ orbital cannot be held bound in this configuration (the exchange integral is repulsive).

The remedy is to consider the alternative coupling, namely, that of the outer pair $(2p3p)\ {}^{3,1}D$ interacting with the $2s$ orbital, for which the following holds:

$$\text{(iv)}\quad \psi[2s(2p3p\ {}^1D)] = (\sqrt{3}/2)(2s2p\ {}^3P^o)3p - (1/2) \times (2s2p\ {}^1P^o)3p,$$

$$\text{(v)}\quad \psi[2s(2p3p\ {}^3D)] = (1/2)(2s2p\ {}^3P^o)3p + (\sqrt{3}/2) \times (2s2p\ {}^1P^o)3p.$$

These linear combinations include the open channel $(2s2p)\ {}^3P^o$ but also the closed channel $(2s2p)\ {}^1P^o$, which contributes to localization via its negative energy exchange integral. The corresponding main correlating configurations are of the type $s(2pp)\ {}^{3,1}D$. These, together with $2s2p^2$ and $2s3p^2$ [while excluding $(2s2p\ {}^3P^o)\overline{p}$], allow convergence to a localized solution which includes, indirectly, part of the contribution of the open channel (Sec. V).

B. Applicability, efficiency, and transparency of Ψ_0

The approach to the calculation and understanding of resonance states that starts with the direct calculation of Ψ_0^k in the form of Eq. (1), has produced a number of results, most of them concerning prototypical cases. In more recent years, other groups have also proceeded with the application of state-specific calculations of Ψ_0^k of ANI resonances or of other autoionizing states of low excitation. For example, in the relativistic calculations of Cai, Beck, and Perger [31] on the Hg $6p^2$ resonances, the expansion for Φ_0^k was chosen to be small, whilst in the nonrelativistic ones of Brage, Froese-Fischer, and Vaeck [32] on two- and three-electron systems, Ψ_0^k was the Φ_0^k itself, represented by a very large expansion. Finally, state-specific calculations of Ψ_0^k, with application to the He$^-$ ${}^2P^o$ resonance studied here, were reported recently by Manby and Doggett [33], who optimized, via the minimax technique, small expansions of spin-coupled wave functions.

Although there are a few extraordinary cases of excited states, such as the H$^-$ dipole resonances, where the application of the MCHF method for the determination of Φ_0^k is impossible and alternative choices of state-specific function spaces are necessary [28], a number of characteristic applications have demonstrated not only the efficiency of computations based on the form (1), but also the possibility one attains of realizing the interplay between the details of electronic structure and the dynamics of decay. This fact provides substantial insight and permits the transfer of computational information between states of similar structures. This contention is supported by a number of results, including those of the present work. An example from the past is the work presented in Ref. [34] on the combined effects of electron correlation and relativity at the Breit-Pauli level for the DES of He of ${}^1D$ and ${}^3D$ symmetries, whose electron pair correlation has analogs in the He$^-$ TES of ${}^2D$ symmetry studied here. These results pertain to the positions and the widths of the five lowest such DES of He, a two-electron system that has been treated extensively by methods employing fixed basis sets [35–37]. The analysis of [34] showed how certain autoionization widths depend crucially on specific correlation configurations belonging to X_{loc}. Furthermore, the results of Ref. [34] differed to some degree from those of [35–37], which also differed among themselves, but were eventually verified by the large scale CCR calculations of Ref. [38].

IV. THE CALCULATION OF Δ, OF γ, AND OF Γ

Once Ψ_0 and E_0 are available, for one or more states of the same symmetry, time-independent [1,2,25–30,34] as well as time-dependent [25] methods employing state-specific wave functions have been applied for the addition of the open channel function spaces that were excluded by projection or construction from Ψ_0. Through these methods, one can compute the partial and total shifts δ_i and Δ and the partial and total widths γ_i and Γ without or with multistate and multichannel coupling.

The continua that are considered here are described by a single free electron. However, in general, the TES can decay via two-electron emission as well. The proper calculation of the rates of such processes requires the possibility of computing pair correlations in the continuous spectrum. (Of course, the immediate approximation is to use a product of two scattering orbitals). A theory for doing so, using a Ψ_0 and an expansion over products of square-integrable complex orbitals, was presented in Ref. [39], with application to the rates of double photoionization of the $1s^2\ {}^1S$ state of H$^-$ and He and of the $1s2s2p\ {}^4P^o$ state of He$^-$. In the present treatment, only the widths for single electron ejection, which is of course dominant, are computed. The aim is to demonstrate the limits of the method within the independent-channel approximation (ICA). As it turns out, the total width is close to the one obtained by the CCR method, [24], where interchannel coupling is included.

For an isolated resonance, such as the ones studied here, in the time-independent framework its complex energy satisfies the transcendental equation

$$z - E_0 - A(z) = 0, \quad z \text{ is complex}, \tag{2}$$

where $A(z)$ is the self-energy of the state [1]. To a very good approximation, Eq. (2) yields the resonance energy as

$$z_0 = E_0 + \Delta(E) - (i/2)\Gamma(E). \tag{3}$$

Provided each channel *i* is formally separated, the functions Δ and Γ are given, on the resonance energy *E*, by

$$\Delta = \sum_i \delta_i , \quad E = E_0 + \Delta, \quad E \text{ is real}, \tag{4}$$

$$\Gamma = \sum_i \gamma_i . \tag{5}$$

For a polyelectronic resonance state with many open channels, the $\delta_i(E)$ and the $\gamma_i(E)$ depend, in general, on interchannel coupling. However, accounting for this effect is computationally cumbersome, even though methods within the SSA are available and have been applied [27–30]. It is certainly more economic to handle such problems in the ICA. In this respect, formalism and calculations without and with interchannel coupling on the nine-electron $\mathrm{Ne}^+\ 1s2s^2 2p^6\ {}^2S$ inner-hole state [29], where five channels are open, as well as on the $1s3s3p\ {}^4P^o$ DES for $Z = 2-5,10$ [30], where three channels are open, indicate a significant result: When the calculation goes beyond the ICA and accounts for interchannel coupling, the total width (but not necessarily the total shift) remains reasonably constant, even though the partial widths may change to some degree. Therefore, by adopting the ICA, the present calculations were carried out using the expressions for the partial shifts and widths that were used before [2(a)]

$$\mathcal{E} - E_0 - \delta_i(\mathcal{E}) = 0, \tag{6a}$$

$$\delta_i(\mathcal{E}) = \mathrm{P}\int_{\mathcal{E}_i} \frac{|\langle \Psi_0 | H - \mathcal{E} | U_i(\varepsilon)\rangle|^2}{\mathcal{E} - \varepsilon} d\varepsilon, \tag{6b}$$

and

$$\gamma_i(E) = \frac{2\pi |\langle \Psi_0 | H - E | U,(E)\rangle|^2}{1 - \delta_i'(E)}, \tag{7}$$

where $\delta_i'(E)$ is the derivative of the energy shift at the *E* of Eq. (4) P denotes the principal value, ε is the energy variable, and E_i is the threshold energy. The appearance of the (*H-E*) operator rather than *H*, results from the formalism and from the fact that the orbital sets for initial and final states are, in general, nonorthonormal.

$U_i(\varepsilon)$ is the *N*-electron scattering wave function, which, given the detailed description of the localized state provided by Ψ_0, is represented accurately by a symmetry-adapted product of a single or of a two-term core function [e.g., $(1s2s + 1s^2)^1S$, or $(2s^2 + 2p^2)^1S$] with a term-dependent numerical HF continuum orbital for each channel *i*. In important channels, if the polarization of the core is expected to contribute significantly to the phase shift of the HF scattering orbital, we account for it by adding to the potential the polarization potential $V(r) = -\alpha/2r^4$ for $r > r_0$, where α is the polarizability (taken from the literature) and r_0 is chosen just beyond the outer maximum of the one-electron density of the core function.

Once the most important δ_i and γ_i are known, the total shift Δ and width Γ are obtained as their sum.

V. CALCULATIONS OF THE *H* LOWEST ${}^2P^o$ AND ${}^2D$ TES, AND INTERPRETATIONS

In the previous sections, we explained why one of the few known triply excited resonances of He^-, the lowest ${}^2D$, has been the object of controversy, and we indicated how the broader problem of identifying and computing resonance (autoionizing) states is handled in the framework of the SSA. In what follows, we will present results and analysis for the properties of Ψ_0, and concomitant numbers for E_0, Δ, γ_i, and Γ of the $\mathrm{He}^-\ 2s^2 2p\ {}^2P^o$ and $2s2p^2\ {}^2D$ resonances. These states were examined again in order to reveal the principal aspects of their formation and quasistability, to compute their properties and to explain why, even for small ANIs, the approach followed by Chung [7,15,16], which also aims at the establishment of a localized wave function Ψ_0, albeit via a different method, may fail to predict reliably the formation of resonances, with particular exemplar the case of the $\mathrm{He}^-\ 2s2p^2\ {}^2D$ resonance.

A. The $\mathrm{He}^-\ 2s^2 2p\ {}^2P^o$ resonance

Apart from the usual electronic structure requirements associated with the self-consistent correlations of the ‘‘motions’’ of the three electrons, this triply excited resonance reflects a rather easy situation, since its position is known to be below the lowest DES of He, the $2s^2\ {}^1S$ state at 57.8 eV.

1. The calculation of Ψ_0*,* E_0*, and of approximations to them*

We start by listing basic results of Ref. [7]

(1) The statement in p. 2782 of Ref. [7] is that *this* ${}^2P^o$ *resonance is formed by channel coupling*. We will show that this resonance is formed mainly via localization of a single HF configuration, without channel coupling.

(2) Figure 7 of Ref. [7] presents the results of a hierarchy of calculations meant to show how the $\mathrm{He}^-\ 2s^2 2p\ {}^2P^o$ resonance is formed as various channels are added. The first calculation, depicted by $\Psi_1 = \psi(2s2s\ {}^1S)\varphi(p)$, produces a completely repulsive curve as a function of $R = \langle r_1 + r_2 + r_3\rangle$, with the conclusion that in this approximation the three-electron system is completely unbound. According to Table I of [7], the target wave function $\psi(2s2s\ {}^1S)$ consists of 78 terms. According to Eq. 11 of Ref. [7], the orbital $\varphi(p)$ is given by a sum of five Slater orbitals with a variational parameter.

(3) The wave function Ψ_4 of Ref. [7], which contains the sum of the contributions from $(2s2s\ {}^1S)\varphi(p)$, (78 terms), $(2s2p\ {}^1P^o)\varphi(s)$, (72 terms), $(2s2p\ {}^3P^o)\varphi(s)$, (69 terms), and $(2s2p\ {}^1P^o)\varphi(d)$, (72 terms), i.e., 291 terms altogether with optimized $\varphi(l)$ orbitals, has produced a total energy of about -0.7907 a.u. (see p. 2782 of Ref. [7]). We will show that within the SSA the physics is revealed in a much simpler way and that the same energy is obtained with just a six term MCHF wave function, containing the most important orbital excitations from a $2s^2 2p$ HF reference wave function.

Let us relate first to items (1) and (2) above, by considering only the $2s^2 2p$ configuration. The corresponding energy expression is very simple, containing two *I*, two *F* and one *G* Slater-Condon integrals. It was already found in [11] that it is

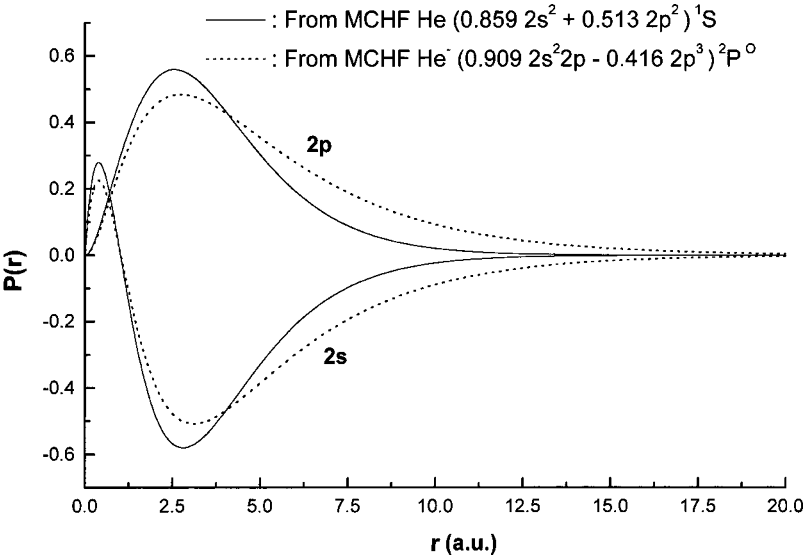

FIG. 1. The $2s$ and $2p$ radial functions of the MCHF wave functions $\mathrm{He}[0.859(2s^2)+0.513(2p^2)]^1S$ (solid line) and $\mathrm{He}^-[0.909(2s^22p)-0.416(2p^3)]^2P^o$ (dotted line). The addition of a p electron to the correlated He ^1S core creates a new self-consistent correlation potential in which the $(2s,2p)$ orbitals of the negative ion are more extended.

indeed possible, even by the analytic SCF method, to obtain valid localized solutions of the corresponding restricted HF equations. We remind the reader that the analytic SCF method is a variational method involving trial orbitals with variable nonlinear parameters. This implies that, in the case of N-electron resonances, as the orbitals are varied a delicate combination of the values of the Slater-Condon integrals produces a local energy minimum. In fact, since the structure of HF theory for bound states is such that its solutions satisfy the virial theorem, one of the criteria of validity of the HF or MCHF solutions for electronic structures with energies in the continuous spectrum that has been used (in conjunction with others) [1,2] is the satisfaction of this relationship. (For atoms and diatomics, the analytic HF method is more complicated and less reliable than the numerical solution of the HF-coupled equations. Indeed, our experience suggests that numerical solutions are achievable for many excited structures of ANIs and, of course, of neutral and ionized atoms. For calculations of excited states of the diatomic molecules $\mathrm{He_2}^+$ and $\mathrm{He_2}^-$ via the numerical solution of the MCHF equations, see Ref. [40].)

When the HF equations are solved for the He$^-$ single configuration $2s^22p\ ^2P^o$ with the $2s$ orbital kept orthogonal to the He ^+1s orbital, there is a valid solution for which the energy is $\varepsilon_{\mathrm{HF}}=-0.742\,78$ a.u. and the orbitals are compact and well behaved, with $\langle r\rangle_{2s}=4.46$ a.u. and $\langle r\rangle_{2p}=3.63$ a.u. (A minimum is also obtained without the $2s$ orthogonality to the He$^+$ $1s$ orbital. Its validity is due to the good one-to-one correspondence between the electronic structure of the state and the numerical stability of the HF solution. However, in general this need not occur, and exclusion of selected lower channels via core orbital orthogonalization is necessary, especially when we include electron correlation [1,2]).

Therefore, there is a state-specific, triply excited $^2P^o$ bound configuration that exists in a local energy minimum without channel coupling. It constitutes the simplest zero-order representation of the exact wavepacket Ψ_0. We note that the He$^-$ $^2P^o$ HF energy is below the HF energy for the He $2s^2\ ^1S$ state, which is $-0.719\,68$ a.u. (For Feshbach P, Q type, and for state-specific calculations on He DES, see Refs. [34,41–43].) However, even if its HF energy were above the HF energy of the He $2s^2\ ^1S$, it is the criterion of localization that would be physically crucial and not the relative position of the two energies. In fact, if one wants to improve the calculation by including the important near-degeneracy mixing $2s^2\leftrightarrow 2p^2$ for both states, then an inversion of levels occurs, since this interaction is stronger in He than in He$^-$, the orbitals of the former being more hydrogenic than those of the latter. Specifically, the MCHF 2×2 wave functions and energies for the two states are

$$0.9094\psi(2s^22p)-0.4160\psi(2p^3),$$

$$E(\mathrm{MCHF})=-0.770\,55\ \text{a.u. for He}^-(^2P^o),$$

$$0.8586\psi(2s^2)+0.5126\psi(2p^2),$$

$$E(\mathrm{MCHF})=-0.776\,76\ \text{a.u. for He}(^1S).$$

As we will see below, when the rest of electron correlation is added for both states, the He $^2P^o$ resonance goes below the He ^1S resonance by 0.61 eV. It is noteworthy that the two sets of $(2s,2p)$ orbitals differ in their size, the ones for He being more compact, as is the case generally when an ANI wave function is compared to that of the parent neutral state. Specifically, for He(^1S):$\langle r\rangle_{2s}=3.34$ a.u., $\langle r\rangle_{2p}=3.13$ a.u. and for He$^-$($^2P^o$):$\langle r\rangle_{2s}=4.12$ a.u., $\langle r\rangle_{2p}=3.91$ a.u. These orbitals are plotted in Fig. 1.

In order to see the occurrence of the local minimum pictorially, we carried out two variational calculations, using just a single Slater orbital for the $2p$ orbital and two choices for the $2s$ orbitals. In the first choice, (=frozen core orbital), the $2s$ orbital is the HF $2s$ of the core state, i.e., of the He $2s^2\ ^1S$. In the second choice, (= relaxed core orbital), the $2s$ orbital is the HF $2s$ of the He$^-$ $2s^22p\ ^2P^o$ calculation, which means that it already contains the self-consistent relaxation due to the presence of the $2p$ orbital. The results of these calculations are plotted in Fig. 2, which depicts the energy of $2s^2p$ as a function of the average value of r of the Slater p

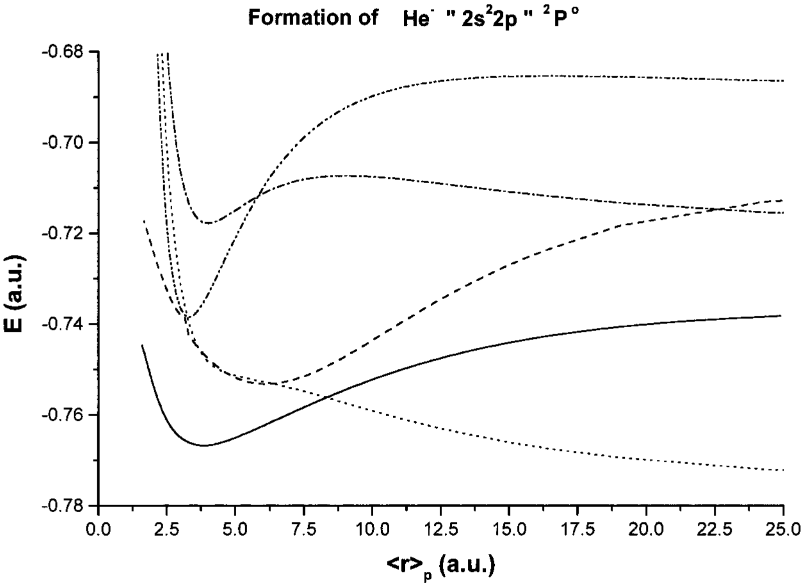

FIG. 2. Plots of the total energy of the He$^-$ $2s^22p$ $^2P^o$ resonance against $\langle r\rangle_p$, the average value of the radius of a one electron function of p symmetry that is coupled to simple two-electron wave functions representing the He ^1S doubly excited state. (Dash dot dot): A single configuration, $2s^2p$, where the $2s$ orbital was obtained from the HF solution of He$^-$ $2s^22p$ $^2P^o$. $E_{\mathrm{min}}=-0.73843$ a.u. at $\langle r\rangle_p=3.30$ a.u. The minimum is deep. (Dash dot): A single configuration, $2s^2p$, where the $2s$ orbital is obtained from the HF solution of He $2s^2$ ^1S. $E_{\mathrm{min}}=-0.71775$ a.u. at $\langle r\rangle_p=4.02$ a.u. The minimum is shallow. (Dot): He$[0.857(2s^2)+0.513(2p^2)]p$ where the $(2s,2p)$ orbitals are from the He ^1S MCHF calculation and p is made orthogonal to $2p$. No binding occurs. (Dash): Two-term, $(2s^2p_1+2p^2p_2)$, $^2P^o$ wave function, where the $(2s,2p)$ orbitals are from the He ^1S MCHF calculation and no orthogonality is imposed among the three p orbitals. $E_{\mathrm{min}}=-0.75316$ a.u. at $\langle r\rangle_1=4.65$ a.u. (fixed) and $\langle r\rangle_2=6.19$ a.u. (Solid): Same as the "dash" case, but the $(2s,2p)$ are relaxed, taken from the He$^-(2s^22p,2p^3)$MCHF calculation. The minimum is deeper than before, reaching $E_{\mathrm{min}}=-0.76671$ a.u. at $\langle r\rangle_1=3.67$ a.u. (fixed) and $\langle r\rangle_2=3.86$ a.u..

orbital. Even with such a simple p orbital, both calculations produce local minima, the one using the relaxed $2s$ HF orbital being lower. Its value is $-0.738\,43$ a.u. and it appears at $\langle r\rangle_p=3.30$ a.u. which is close to that of the (more flexible) numerical HF solution, for which $\langle r\rangle_{2p}=3.63$ a.u. In fact, when two p Slater functions are used and optimized variationally, the local energy minimum is at $-0.742\,74$ a.u., almost identical to the numerical HF value. This result is in accordance with the state-specific approach, since such a calculation constitutes an approximation to an analytic HF calculation in its last cycle, i.e., when the $2s$ orbital has already been optimized and the $2p$ orbital, expressed as $|2p\rangle=\Sigma c_iu_i$, where u_i are Slater orbitals, is varied to minimize the energy.

The conclusion, therefore, is that the He$^{-2}P^o$ resonance is already quasibound at the single-configuration HF level, without any CI or channel coupling.

Given the above fact and items (1) and (2) above, it is instructive to consider the possible reason of why Chung's large calculation with wave function Ψ_1 (78 terms) produces a totally repulsive energy curve as a function of the average value of $\langle r\rangle_p$. (His use of $R=\langle r_1+r_2+r_3\rangle$ is essentially the same thing, since the target functions are frozen). So let us consider the electronic structure of the He $2s^2$ ^1S state. Its overwhelmingly dominant electron-correlation effect is the mixing $2s^2\leftrightarrow 2p^2$. We now carry out two types of variational calculations, using analytic orbitals for the third electron (p orbital) of He$^-$.

In the first, we use one p Slater orbital, orthogonal to the $2p$ of the 2×2 MCHF He wave function, and form a three-electron wave function, as Chung does with his 78-term target function. Specifically, we form $\Psi(a2s^2+b2p^2)p_1$ and follow the total energy by varying the exponent of the p_1 Slater orbital. No binding takes place. The corresponding repulsive curve is shown in Fig. 2. It is the result of the repulsive interaction between the extra p electron and the $2p^2$ term in the target function, *to which it was kept orthogonal*. Such a repulsive interaction must also dominate the calculation of Chung [7], where the frozen orbital $2p^2$-type term is included in the 78-term expansion, and where the extra p orbital is kept orthogonal to the target function. In the second type of calculation, we consider each of the two configurations separately, we form $a\Psi(2s^2p_1)+b\Psi(2p^2p_2)$ and very each of the two p Slater orbitals separately. Now, the p_1 and p_2 orbitals are not restricted to being orthogonal either to the $2p$ HF orbital of the target wave function or between them. The solution of this two-configuration case requires a nonorthonormal CI (NONCI) calculation and shows that binding does occur, since the role of the three-electron configuration $2p^2p_2$ is to improve the single-configuration result. The corresponding energy curve with the local minimum is also shown in Fig. 2. The plot is one dimensional, with the $\langle r\rangle_p$ of the p_1 orbital being kept at its optimal value, 4.65 a.u. For this calculation, the energy minimum is at $-0.753\,16$ a.u.

(a) State-specific few-term wave functions vs the 291-term wave function of Ref. [7]. Having established the localization

of the state at the zero-order level, we can improve the wave function and the energy by adding electron correlation configuration that do not destroy localization. By choosing the important configurations in a hierarchical manner, we first obtain multiconfigurational representations of the Φ_0^k of Eq. (1). In this first stage, the convergence of the calculation toward the accurate final result is fast and physically transparent. We give an example: The significant orbital excitations from the $2s^2 2p$ reference configuration are: $2s \rightarrow d$, $2s^2 \rightarrow p^2$, and $2s2p \rightarrow sp$. Within a minimum size MCHF scheme, the corresponding configurations are: $2s^2 2p$, $2p^3$, $(2s2p)^3 P^o 3d$, $(2s2p)\ {}^1P^o 3d$, $2s(3s3p)\ {}^3P^o$, and $2s(3s3p)\ {}^1P^o$. When this six-term MCHF calculation is done, the energy is $-0.790\,98$ a.u., which is exactly the same as the energy obtained in Ref. [7] with a 291-term wave function [item (3) above].

The result based on the six-term Φ_0^k can be improved by augmenting judiciously the reference space. Indeed, a 35-term Φ_0^k gave $E_0(\Phi_0^k) = -0.798\,68$ a.u., or 52.27 eV above the He ground state. The measurements of Refs. [17,18] gave the position at 57.22 ± 0.04 and 57.19 ± 0.03 eV, and the large-scale CCR calculation of Bylicki and Nicolaides [9], (which includes the full contribution of the open channels), gave $E = 57.205$ eV.

The results above provide yet another example of the spectacularly good convergence toward the accurate energy and electronic structure of MES and of inner-hole states that is achieved when state-specific MCHF calculations, with suitably chosen few configurations, are carried out.

(b) Addition of X_{loc} and final NONCI energy. We now continue the calculation of Ψ_0 by adding terms belonging to X_{loc}^k. Since very good convergence has already been achieved by the 35-term Φ_0^k, the calculation of this part is very slowly convergent, in spite of the fact that the corresponding variational calculation is done via NONCI, a characteristic feature of many state-specific calculations of atomic and molecular states [44]. Eventually, a 588-term Ψ_0 was computed, nearly exhausting the full space of single, double, and triple orbital excitations. The corresponding energy is $E_0\ (\text{He}^-\ {}^2P^o) = -0.80128$ a.u. or 57.203 eV above the He ${}^1S$ state. In fact, in order to reach the full CI limit, we resorted to a $1/M$ extrapolation of E_0, where M is the number of configurations in Ψ_0, for $M = 35$, 150, 355, and 683. The extrapolated value is

$$\begin{aligned} E_0(\text{He}\ {}^{-2}P_0) &= -0.802\,411 \pm 0.000\,133\ \text{ a.u.} \\ &= 57.172\ \text{ eV }\ above\ \text{ He }{}^1S. \end{aligned} \tag{8}$$

(c) Comment. One might argue that, even though the approach advocated in [7,15,16] does not produce binding for the He$^-$ $2s^2 2p\ {}^2P^o$ resonance without *channel coupling* and large core wave functions, eventually Chung's full calculation leads to the same final conclusion as that of the present analysis, namely, that this resonance exists, with an energy around 57.2 eV. In other words, one could argue that even though the economy and the physical picture of the two methodologies are different, the end result is the same. However, this would not be a good argument for a number of reasons, of which the most interesting is offered by the example of Sec. V B, i.e., the issue of the existence or not of the He$^-$ $2s2p^2\ {}^2D$ resonance, whose background was already presented in Sec. II.

2. The calculation of γ_i of Γ, and of Δ

Experimentally, the formation and decay of the He$^-$ $2s^2 2p\ {}^2P^o$ resonance in the three inelastic channels $1s2s\ {}^1S$, $1s2s\ {}^3S$, and $1s2p\ {}^1P^o$ was observed already in the 1960s by Simpson, Menendez, and Mielczarek [45]. A recent measurement and discussion of the relative rates of decay into the He $1s2s\ {}^{1,3}S, 1s2p\ {}^{1,3}P^o$ channels was reported in Ref. [21]. An important measurement was also made in 1969 by Burrow and Schulz [46], who recorded the decay by two-electron emission. However, no measurement of these partial widths have been reported. On the other hand, the total width was measured some time ago by Quemener, Paquet, and Marmat [20] as 90 ± 14 meV while a more recent unpublished measurement by van den Brink [17] gave 70 ± 10 meV.

As regards theory, the first result, 2.4 meV, is that of Smith *et al.* [47] from close-coupling calculations. More than 20 years later, Bylicki and Nicolaides [9] reported a width of 71 meV, obtained from CCR calculations that include, in principle, the contribution of all open channels, having one as well as two free electrons. More recently, Smith *et al.* [44] and Manby and Doggett [33] also published results of calculations of Γ. Zhang and Chung [48] reported $\Gamma = 68.5$ meV, obtained by a method using real and complex coordinates on which we commented in Ref. [1(c)]. Manby and Doggett [33] reported $\Gamma = 82$ meV, obtained by using the golden rule and the ICA, with Ψ_0 being a state-specific two-term spin-coupled wave function with flexible orbitals. The scattering functions were approximated by a set of L^2 orbitals. It is noteworthy that they gave as an estimate of the partial widths for two-electron emission the value 3.7 meV.

The results for the partial and total widths of [9,33,48] and of the present work are presented in Table I. Our calculations were done according to the method presented in Sec. IV. The following open channels were considered: $1s2s\ {}^3S\ \varepsilon p$, $1s2s\ {}^1S\ \varepsilon p$, $1s2p\ {}^3P^o\ (\varepsilon s, \varepsilon d)$, and $1s2p\ {}^1P^o(\varepsilon s, \varepsilon d)$. The calculation of the He ${}^1S$ core involved the simultaneous optimization of the two roots $(1s2s + 1s^2)^1S$.

Judging from the theoretical results of Refs. [9,33,48] and of the present work ($\Gamma = 69$ meV), and from the experimental value of van den Brink [17], and if we take for the partial width of two-electron emission the value 2–4 meV (not included in our calculation), we come to the conclusion that the theoretical prediction for Γ is in the range 68–74 meV.

On the other hand, there is some discrepancy among the results of Refs. [33,48] and this work as regards the partial widths. In our calculation, the largest contribution comes from the $1s2s\ {}^1S$ ($\gamma = 21$ meV) and $1s2p\ {}^3P^o$ ($\gamma = 34$ meV) channels, whereas in those of Zhang and Chung [48] the γ of the ${}^3P^o$ channel is dominant (41 meV) and in those of Manby and Doggett [33] it is the ${}^1P^o$ and the ${}^1S$ channels that dominate [$\gamma({}^1P^o) = 26$ meV, $\gamma({}^1S) = 28$ meV].

TABLE I. Partial and total widths (in meV) for the He^- $2s^2 2p\ ^2P^o$ resonance state, obtained in this work, Eqs. (1)–(7), in earlier calculations [9,33,48] and in measurements [20]. For our results we used the reduced 1 a.u.(He) = 27.207 7 eV.

	Theory				Experiment	
Channels	This work	[9]	[33]	[48]	[20]	[a]
$1s2p(^3P^o)\varepsilon s$	33		13	41		
$1s2p(^3P^o)\varepsilon d$	4			3		
$1s2p(^1P^o)\varepsilon s$	10		26	13		
$1s2p(^1P^o)\varepsilon d$	0.6			0.4		
$1s2s(^3S)\varepsilon p$	0.4		11	0.6		
$1s2p(^1S)\varepsilon p$	21		28	13		
Total	69	71	82	69	90±14	70±10

[a] Unpublished result of van den Brink, see Ref. [17]

As regards the total energy shift Δ we estimate that its magnitude is about 30 meV. This is obtained from Eq. (4) and the fact that, for this state, we estimated that interchannel coupling reduces by about 40–50% the value from the ICA. Therefore, using Eq. (8); the total energy E (SSA) of this state is given by

$$E(\mathrm{SSA}) = E_0 + \Delta = (57.172 + 0.030)\ \ \mathrm{eV} = 57.202\ \ \mathrm{eV}. \tag{9}$$

Given the other theoretical and experimental results, (see our references and tables in Refs. [9,48]), we suggest that the position of this resonance state is at $E = 57.204 \pm 0.005$ eV.

B. The He $2s2p^2\ ^2D$ resonance

As we discussed in Sec. II, the existence of such a resonance has been disputed in a series of papers during the last two decades [7,15,16,22], culminating in the latest one of 1998 [7]. This fact has created confusion as to the nature, formation and observation of this state (e.g., [17,21]) and as regards the theory and computation of resonance states of polyelectronic systems in general. Furthermore, Chung has claimed (e.g., [15,22]) that earlier calculations by one of us (C.A.N.) of the Ψ^o of the He^- $2s2p^2\ ^2D$ resonance are invalid, because of the inclusion of terms of the type $2s^2d$ and $2p^2d$. [These correspond to the OCL configurations discussed in Refs. [1,2] and in Sec. II. We return to this issue in paragraph (3′) below.]

In what follows, we will examine the question of the ^2D resonance formation along the lines discussed above for the He^- $^2P^o$ resonance, and we will show that the related objections of Refs. [7,15,16,22] are without foundation. The He^- ^2D resonance is indeed formed at 58.3 eV, with a width in the range 40–60 meV. This conclusion is based on the results of Refs. [2,9] and the present ones, obtained with simple as well as with well-correlated wave functions, whose analysis reveals the constitution and the properties of its localized part Ψ_0.

We list basic results of Ref. [7]:

(1) On 2784 of Ref. [7], it is stated: "Judging from the experimentally observed position (of the ^2D structure), $\psi(2s2p\ ^3P^o)\varphi(p)$ is obviously the most important channel. However, this channel is not favorable in forming a ^2D resonance since the exchange integral between the outermost electron and the target is positive. Hence, one should not be surprised to find the result for Ψ_1 in Fig. 10 (which shows that the energy curve as a function of $R = \langle r_1 + r_2 + r_3 \rangle$ is repulsive)."

(2) The coupling of many channels, containing hundreds of terms, do not change the repulsive nature of the energy curve (Figs. 10 and 11 of [7]), leading Chung to his conclusion about the nonexistence of the He^- ^2D resonance.

Let us start by considering only the $2s2p^2\ ^2D$ configuration. As we already stated in Sec. III, the corresponding restricted HF equations can be solved numerically to produce a localized solution, with or without orthogonality of the HF$2s$ orbital to the $\mathrm{He}^+ 1s$ hydrogenic orbital. The $2s$ and $2p$ orbitals are compact, with $\langle r \rangle_{2s} = 4.1$ a.u. and $\langle r \rangle_{2p} = 4.4$ a.u. This orbital wave function constitutes the simplest zero-order representation of the ^2D resonance, with an optimized energy that is a local minimum inside the continuum. The remaining of the calculation toward the determination of Ψ_0 involves the addition of configurations which, even though they are optimized variationally, do not destroy the localization of the trial function.

The discussion that follows has three parts. In Sec. V B 1 we present results based on simple wave functions in order to provide pictures of the energy minima attained in the continuum as the radial function of the third electron is varied. In Sec. V B 2 we present our results for the character of Ψ_0 and for the value of E. In Sec. V B 3 we present the results for Γ and the partial widths. All the results establish beyond doubt the existence of this resonance, while demonstrating how the SSA addresses, in general, the problem of understanding the formation and the properties of resonances of polyelectronic atoms.

1. Local energy minima and their relation to simple configurational functions without and with relaxation and channel coupling

We will discuss three notions:

(1) The notion of orbital flexibility in the single configuration $(2s2pp')^2D$, implemented via a nonorthogonal p orbital optimized variationally.

(2) The notion of correcting the localized orbital wave function $(2s2p\ ^3P^o)p_1$ via coupling with the channels $(2s2p\ ^1P^o)p_1$, $(2p3d\ ^3P^o)p_2$, and $(3s3p\ ^3P^o)p_3$. The p_i ($i = 1, 2, 3$) are analytic (Slater) orbitals whose exponents are varied. They are not orthogonal among them or to the $2p$ and $3p$ orbitals of the target functions.

(3) The notion of *open-channel-like* configurations $(a2s^2 + b2p^2)d$, obtained self-consistently from an MCHF calculation and contributing to the stability of the wavepacket.

(1′) We already mentioned the fact that the He^- $2s2p^2\ ^2D$ single configuration Hartree-Fock equations have

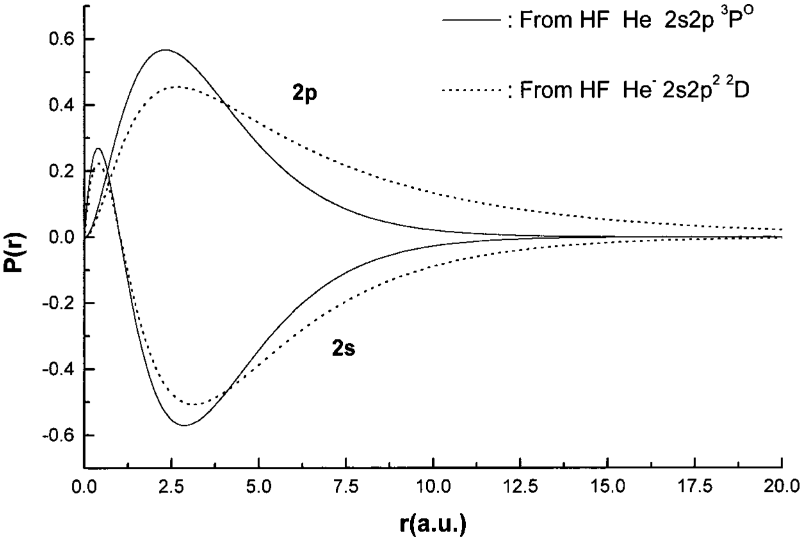

FIG. 3. The $2s$ and $2p$ orbitals from the HF calculations of the He $2s2p\ ^3P^o$ (solid line) and He$^-$ $2s2p^2\ ^2D$ (dotted line) resonance states.

a perfectly acceptable localized solution. This implies that as the orbitals are varied in the self-consistent field, the total energy reaches a minimum (-0.708 a.u) with respect to these variations. We shall call the $(2s,2p)$ orbitals from this HF calculation the *relaxed orbitals*, and will distinguish them from the HF$(2s,2p)$ orbitals of the He $2s2p\ ^3P^o$ state, which will be called *frozen orbitals*. Indeed, these two sets of orbitals are different, as can be seen from Fig. 3.

Now let us consider the concept of *(N−1)-electron target plus extra electron* that characterizes the approach followed in Refs. [7,15,16]. This implies that we choose a core He wave function of $^3P^o$ symmetry to which we couple a p orbital representing the third electron. Chung [7] used a 69-term $^3P^o$ wave function and found no binding of the third electron. We will use only one configuration, $(2s2pp_1)^2D$, whose proper electron coupling yields two terms, the $(2s2p\ ^3P^o)p_1$ and the $(2s2p\ ^1P^o)p_1$, and will show that the binding indeed takes place, provided these zero-order configurations consist of flexible orbitals, i.e., of the relaxed $(2s,2p)$ orbitals and a simple Slater p_1 orbital that, however, is not orthogonal to the $2p$ one. The binding is depicted as the occurrence of a local minimum of the total energy of $(2s2pp_1)^2D$, as the average value of the radius of $p_1, \langle r\rangle_p$, is varied. (That is, the nonlinear parameter of the Slater orbital is varied.)

Before we show the relevant results, it is useful to relate the meaning of the $(2s2p\ ^{3,1}P^o)p_1$ configuration to the state-specific electronic structure theory. When the SSA is considered, the implication is that the self-consistently obtained $2s2p^2\ ^2D$HF configuration can be adopted as the reference localized wave function. Even though the two orbitals $(2s,2p)$ are optimized self-consistently, it is known from our previous work on He$^-$, as well as from previous theory of the interplay between atomic structure and atomic spectra (see the reviews [44,49]), that for $sp^2\ ^2D$ structures, electron correlation causes significant polarization of the $2p$ orbital, even in neutral states. This effect appears as CI with configurations of the type $sp^2\ ^2D$. For example, the strongly perturbed Al ^2D spectrum [27] is characterized mainly by CI of the type $3s3p^2 \leftrightarrow 3s3pnp(n>3) \leftrightarrow 3s^2md$, $\varepsilon d \leftrightarrow 3p^2md \leftrightarrow 3pnpmd(m=3,4,...)$, with the $3s3pnp$ configurations corresponding to observed resonances [50]. A way to account for most of this polarization is to allow the two $2p$ orbitals of the $2s2p^2\ ^2D$ configuration to be different (= unrestricted HF theory). A practical approximation to this, which is relevant to the present discussion, is the use of the $(2s2p\ ^{3,1}P^o)p_1$ two-term wave function, with separately optimized nonorthogonal orbitals.

Figure 4 presents two energy curves of the two-term $(2s2p\ ^{3,1}P^o)p_1\ ^2D$ wave function as a function of $\langle r\rangle_p$, the average value of r for p_1. It is repulsive when the p_1 function is orthogonal to the $2p$ orbital, regardless of whether the latter is taken from the He $2s2p\ ^3P^o$ "target" (frozen orbitals) or from the He$^-$ $2s2p^2\ ^2D$ configuration (relaxed orbitals). A repulsive curve is obtained as well when the core orbitals are frozen and p_1 is nonorthogonal. Only when the p_1 is free to be nonorthogonal to the $2p$ of the $2s2p^2$ configuration does the local minimum appear at $E=-0.705\,47$ a.u. with $\langle r\rangle_p=3.68$ a.u. In fact, when the p space is made more flexible by adding one more Slater orbital, the minimum is deepened to $E=-0.70935$ a.u., which is below the restricted HF value ($-0.708\,09$ a.u.). This is simply because this calculation approximates an unrestricted HF calculation of the $2s2p2p'$ type with nonorthogonal orbitals.

The existence of the local energy minimum, even with such simple (but physically relevant) functions for the He$^-$ (target $^3P^o$) $p_1\ ^2D$ "channel," contradicts the claim of Refs. [7,15,16]. It also constitutes an example whereby it becomes clear that the state-specific strategy toward the solution of certain problems in excited states not only is more economical and transparent but also necessary [44].

$(2')$ We now proceed to see what happens if we add other "channels" to the results of $(1)'$. Does the local energy minimum survive or is it destroyed?

As we already reported in Ref. [2(a)], the He $2s2p\ ^3P^o$ resonance state is overwhelmingly dominated by three configurations, the $2s2p$, $2p3d$, and $3s3p$, provided they are obtained self-consistently by the MCHF procedure, in which case they contain the contributions of higher-lying excita-

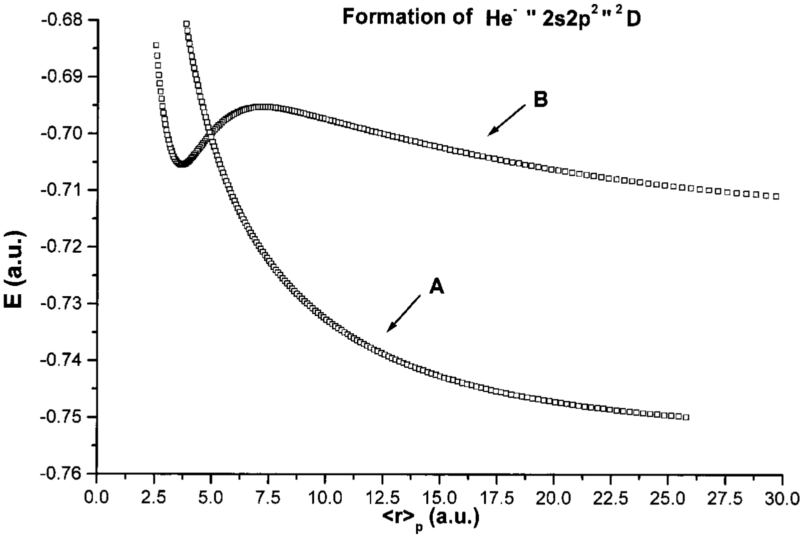

FIG. 4. The total energy of the He^- ^2D resonance state, represented by one configuration, $2s2pp$, coupled as $(2s2p\ ^{3,1}P^o)p$, against $\langle r\rangle_p$, the average value of the radius of the variational orbital p. (a) The repulsive curve corresponds to the case where the p orbital is orthogonal to the $(2s,2p)$ orbitals, regardless of whether these are relaxed or frozen. (b) The local minimum appears when the $(2s,2p)$ are relaxed (taken from the He^- $2s2p^2\ ^2D$ calculation) and the p orbital is left nonorthogonal to the $2p$ one.

tions. The corresponding localized wave function is

$$\Phi_{\mathrm{MCHF}}(\mathrm{He}\ ^3P^o)=0.992\psi(2s2p)-0.118\psi(2p3d)$$
$$-0.049\psi(3s3p), \qquad (10)$$

with $E=-0.76093$ a.u. or 58.300 eV above the He^1S,[1 a.u.(He)=27.2077 eV], which is in excellent agreement with the experimental values of Gosselin and Marmet [6] (58.309±0.003 eV) and of Mannervik [51] (58.312 ±0.003 eV). The remaining small part of the localized energy (negative) is essentially balanced out by the energy shift Δ that is positive.

Given the above constitution of the He $^3P^o$ resonance state, we consider the coupling of four "channels": $(2s2p\ ^3P^o)p_1$, $(2s2p\ ^1P^o)p_1$, $(2p'3d\ ^3P^o)p_2$, and $(3s3p\ ^3P^o)p_3$, with all the p orbitals kept nonorthogonal. The p_1, p_2, and p_3 orbitals are analytic Slater orbitals that are varied to minimize the total energy from a 4×4NONCI. The $(2s2p\ ^{3,1}P^o)$ orbitals are the relaxed numerical orbitals from the calculation of $2s2p^2\ ^2D$. The $2p'$, $3s$, $3p$, and $3d$ orbitals are the frozen numerical MCHF orbitals from the calculation of the He $2s2p\ ^3P^o$ state (10). Figure 5 shows the two-dimensional energy surface as a function of the average r of p_2 and p_3, when p_1 is kept fixed at its optimal value. It is seen that channel-coupling sustains the local energy minimum, which is now found to be at $E=-0.71252$ a.u. The average values of r for the three optimized p orbitals are, $\langle r\rangle_1=3.70$ a.u., $\langle r\rangle_2=4.74$ a.u. and $\langle r\rangle=5.56$ a.u.

(3′) For many-particle systems, the theory of resonance states is based, in one form or another, on the formal separation of the full space into two parts, one representing bound components and one representing scattering ones. The proper handling of the formal mixing of such components

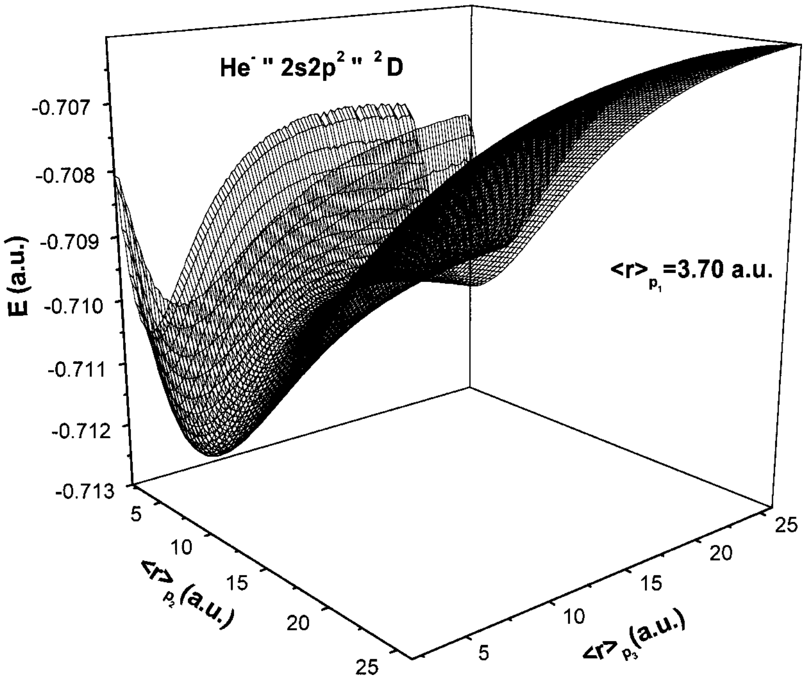

FIG. 5. A two-dimensional energy surface of the He^- ^2D localized part, as a function of the average radius of two Slater orbitals, p_1 and p_2. These orbitals enter in the state-specific 4×4 nonorthonormal configuration interaction (NONCI) calculation, with $(2s2p\ ^3P^o)p_1$, $(2s2p\ ^1P^o)p_1$, $(2p3d\ ^3P^o)p_2$, and $(3s3p\ ^3P^o)p_3$. When $\langle r\rangle_1$ is fixed at its optimal value, 3.70 a.u., the energy minimum is at $-0.712\,52$ a.u. with $\langle r\rangle_2=4.74$ a.u. and $\langle r\rangle_3=5.56$ a.u..

leads to the phenomenology of resonance states (e.g., phase shifts, time delay, lifetime, cross-section). On the other hand, it is equally important for the physics of real polyelectronic atoms and molecules to go beyond phenomenology and to be able to compute from first principles the intrinsic properties of resonances.

In the exchange of views [1(c),22] on the validity of the SSA calculation of the $\mathrm{He}^- \, 2s2p^2 \; ^2D$ resonances, Chung [22] objected to the fact that the calculations in Refs. [1,2] included correlation configurations of the type $(2s^2+2p^2)d$, since the $\mathrm{He}2s^2 \; ^1S$ state lies energetically lower, and, therefore, it gives rise to an open channel. Although we discussed this issue in Refs. [1,2], we return to it here, in order to provide additional numerical information which is related to Chung's stated question (p. 695 of Ref. [22]): "My question about Nicolaides' $2s2p^2 \; ^2D$ calculation is: why not include the other $2s^2nd$ and $2p^2nd$ orbitals with $n=4$, 5, 6,...? Do these orbitals in some way conflict with the "state-specific theory" whereas $3d$ does not? If we do include these *nd* orbitals into the wave function, the lowest root of the energy will fall towards the $2s^2$ [more precisely, $(2s^2+2p^2)^1S$] threshold. Therefore, the solution Nicolaides obtained was the result of an incomplete calculation."

The general answer to the above remarks can be found in pp. 460–465 of Ref. [1(b)] and p. 692 of Ref. [1(c)]. In Ref. [2(a)] we introduced the name *open channel-like* configurations, in order to underline their distinct features. Here we provide additional information in order to complete the arguments of the present paper.

The pair correlation of the two *p* electrons of the HF configuration $\mathrm{He}^- 2s2p^2$ leads to virtual excitations representing both "*localized*" and "*asymptotic*" components of the resonance wave function. The asymptotic components derive their existence from the energetically open channels. However, as we argued in Refs. [1,2], when carrying out either a variational calculation with carefully observed constraints, or, better, a numerical solution of the appropriate MCHF equations, it is possible to incorporate part of the space belonging to an open channel into the localized component. In other words, the localized wavepacket in the continuous spectrum representing the state at $t=0$ [1,25] need not be constructed only by functions corresponding to closed channels. Using the language of configurations, in the present case there are three open channels (two thresholds) with respect to the HF energy of the $2s2p^2$ configuration, which were shown in (i)–(iii) of Sec. III A. Since the HF energy of the $2s2p^2 \; ^2D$ configuration is above the energy of the He $2s2p \; ^3P^o$ threshold, the "problem" stressed by Chung ought to arise also with the $(2s2p \; ^3P^o)p$ variational calculations. Yet, we already saw that, with $(2s,2p)$ orbitals that have incorporated the effect of relaxation, a variational calculation with nonorthogonal orbitals leads to well-converged local energy minima when a Slater orbital of *p* symmetry is optimized. The energy of the three-electron ANI does not collapse to the He $2s2p \; ^3P^o$ threshold when one more *p* function is added. It is simply improved toward a convergence limit, just like in any ordinary case of a bound state.

As regards the $(2s^2)d$ channel, in Refs. [1(c),2(a)] we discussed its significance and its contribution to the localized part via MCHF calculations that include the $2s^23d$ OCL configuration. As with any variational calculation of the MCHF type, it is not necessary to include the $n=4$, 5, 6,... correlation orbitals in order to achieve a sufficiently accurate convergence within the local minimum. Even in a ground state calculation, it has been known for decades that such variationally optimized orbitals include most of the contribution from the infinity of higher bound and scattering states. In order to support this statement for the present example, we close by listing a series of new results from MCHF calculations on the ^2D state.

A 2×2 MCHF calculation with $2s2p^2$ and $2s^23d$ configurations gives $E(2\times2)=-0.71989$ a.u., with $\Phi_{\mathrm{MCHF}}=0.957\psi(2s2p)^2-0.290\psi(2s^23d)$. Again we stress that this "$3d$" bound orbital represents a one-electron wavepacket containing major contributions from the εd open channel, but does not represent the asymptotically free-electron function of this channel. The latter is computed in a separate, scattering-type calculation, where the εd scattering function is obtained numerically from a frozen core $^1S(\mathrm{He}\, 2s^2+2p^2)$ potential.

Now we add the important $2s\rightarrow d$ correlation, which is present in the $2s2p^2$ configuration. A 5×5 MCHF calculation gives $E(5\times5)=-0.73696$ a.u., with

$$\begin{aligned}\Phi_{\mathrm{MCHF}}= {} & 0.918\psi(2s2p^2)-0.294\psi(2s^23d)\\ & -0.242\psi[(2p^2\;^3P)3d]-0.107\psi[(2p^2\;^1S)3d]\\ & +0.025\psi[(2p^2\;^1D)3d].\end{aligned}$$

The orbitals are compact, with $\langle r\rangle_{2s}=4.02$ a.u., $\langle r\rangle_{2p}=4.12$ a.u., and $\langle r\rangle_{3d}=5.83$ a.u. The virial relation gives 2.03.

Finally, we perform a large (and difficult) MCHF calculation with 48 and 49 terms, without and with a $2s^24d$ configuration. The results are nearly the same: $E_0(48)=-0.75601$ a.u. and $E_0(49)=-0.75606$ a.u. (58.43 eV above the He ^1S state). This fact proves that the addition of the $4d$ orbital does not bring about a result supporting the concern and prediction of Chung. Localization and energy stability hold well. The coefficient of the $2s^24d$ OCL configuration is only 0.0148, whilst that of the $2s^23d$ OCL configuration is -0.1954. A comparison of this $3d$ orbital to the HFεd scattering orbital obtained in the $\mathrm{He}(2s^2+2p^2\;^1S)$ core potential, shows that they look quite different. (Fig. 6). (Their overlap is only 0.022.)

We stress that the incorporation of the $2s^23d$ configuration into the MCHF calculation not only does not cause harm but it facilitates convergence. Furthermore, it brings in the response of the bound closed channel components to the open channel in a self-consistent manner, something which is still a *desideratum* for all approaches that are based on the concept of *(N−1)-electron target state plus extra electron*.

2. Results for the character of Ψ_0 and for the value of E_0

The Φ_{MCHF} (49) discussed above, contains the major components of the $\mathrm{He}^- \; ^2D$ resonance. The most important

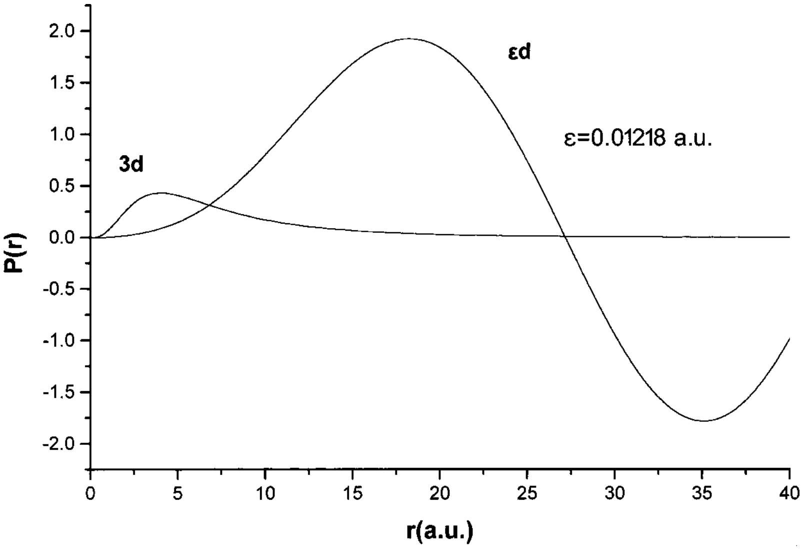

FIG. 6. Comparison of the $3d$ orbital in the open channel-like (OCL) configuration $2s^2 3d$, included in a 49-term MCHF calculation of the He^- $2s2p^2\ {}^2D$ resonance state, with the scattering εd orbital obtained for $\varepsilon = 0.012\,18$ a.u., the energy difference of the ${}^2D$ MCHF solution from the exact energy of the He $2s^2\ {}^1S$ threshold. The εd orbital was obtained numerically in the core potential of $\mathrm{He}(2s^2 + 2p^2)^1S$. The $3d$ orbital is localized, having no resemblance to the εd scattering orbital.

ten configurations and their coefficients are listed in Table II. Notice that from the point of view of the discussion on electron correlation of the previous sections, the following orbital excitations from the $2s2p^2$ configuration acquire the highest weight

$$2p \rightarrow p,f, \quad 2s \rightarrow d, \tag{vi}$$

$$2p^2 \rightarrow 2sd, 3p^2. \tag{vii}$$

In fact, a careful study of the constitution of this wave function, together with energy considerations, led to the conclusion of the existence of a correlation-induced $\mathrm{He}^-\ {}^2D$ triply excited resonance very close to the $2s2p^2\ {}^2D$ state. This prediction and its connection to the measurements of Gosselin and Marmet [6] will be discussed in Ref. [8].

Having established localization with a sufficiently accurate energy, -0.75606 a.u., via the 49-term MCHF calculation, we add the remaining localized correlation function space and compute the energy $E_0(\Psi_0)$, as well as the energy shift Δ in order to obtain the final result $E = E_0 + \Delta$. This E is then compared to the energy of the He $2s2p\ {}^3P^o$ state. For the latter we take as accurate values the two experimental ones [6,51] already cited, and the computed ones via the CCR method by Ho [52] and by Lindroth [53], both of which are -0.760492 a.u. (58.312 eV above the He ground state).

TABLE II. The ten most important localized configurations comprising the He^- $2s2p^2\ {}^2D$ resonance state, obtained numerically from a 49-term multiconfigurational Hartree-Fock calculation.

Configuration	Weight
$2s2p^2$	0.8802
$(2s2p)^1P^o 3p$	−0.2659
$2s3p^2$	−0.2342
$2s^2 3d$	−0.1954
$3d(2p^2)^3P$	−0.1267
$3d(2p^2)^1D$	0.1107
$3s(2p3p)^1D$	−0.0861
$2s(2p4p)^3D$	0.0495
$(2s2p)^3P^o 4f$	0.0270
$2s^2 4d$	0.0148

Correction to the energy via NONCI of separately obtained state-specific correlated Ψ_0. For low-lying states, the notion of an isolated state is, in general, valid. Therefore, the direct, state-specific calculation of its energy can be done by following the strategy described thus far in this paper. However, with increasing excitation energy the density of resonance states increases. As a result, for the same symmetry, the spectrum contains closely lying or overlapping resonances. The handling of such cases, say of triply excited resonances very near others of different electronic structures, is in principle a complex problem for which very little has been done. In a calculation of any scheme, the localized function spaces representing different states interact either directly or via the continuous spectrum. For example, such a multistate interaction was shown to have spectroscopic impact in the case of the Al ${}^2D$ spectrum [27,50].

During the present study of He^- resonances, analysis of the correlated wave functions with small or large expansions eventually led us to the conclusion that there are two closely lying ${}^2D$ states around 58.3 eV. The lowest one is the one on which we reported here. The next one is discussed in Ref. [8]. Because of the high accuracy for the total energy that we aimed at, so as to decide whether the E of the He ${}^2D$ state is below or above the He $2s2p\ {}^3P^o$ energy, the aforementioned small effect of the influence of the closely lying second ${}^2D$ resonance on the first one, and vice versa, was taken into account here by a scheme that is explained below. It is general enough to be used in many such cases of interacting excited states in atoms and molecules. In fact, a version of it was first applied some time ago to excited states of twisted butadiene and ethylene, see Refs. in Ref. [44].

First, two separate large state-specific NONCI calculations were carried out for the two states, using as reference wave functions the MCHF solutions with 49 configurations. Systematic increase of the size of Ψ_0, via the inclusion and optimization of one-, two-, and three-electron virtual excitations, finally led to an expansion of 778 symmetry-adapted

TABLE III. Partial and total-energy widths and shifts (in meV) for the He^- $2s2p^{2}\,{}^{2}D$ resonance state, obtained in this work, in earlier calculations [9] and in measurements [6,20]. For our results we used the reduced 1 a.u.(He) = 27.2077 eV.

	Widths						
	Theory			Experiment			Shifts
Channels	This work	[9]	[47]	[20]	[6]	[a]	This work
$2s^2\varepsilon d$	6						-2
$1s2p(^3P^o)\varepsilon p$	10						6
$1s2p(^1P^o)\varepsilon p$	1						7
$1s2s(^3S)\varepsilon d$	11						5
$1s2s(^1S)\varepsilon d$	5						3
Total	33	49	25	50 ± 20	59 ± 4	40 ± 10	19

[a] Unpublished result of van den Brink see Ref. [17]

configurations for each of the lowest two ^2D triply excited resonances. These two solutions were then diagonalized in a full NONCI calculation. This diagonalization corrects slightly the two wave functions and their energies, by incorporating the remaining of the details of the higher order effects that were not picked up by the function space of each state separately.

The total energy for the first ^2D root computed in this way is

$$E_0(^2D) = -0.761\,990 \quad \text{a.u.}, \tag{11}$$

which is below the He $^3P^o$ energy. However, the final energy is obtained after the calculation of the energy shift Δ. The results for the partial shifts and widths, obtained according to the method of Sec. III, are presented in Table III. The total shift comes out as 19 meV $(6.98 \times 10^{-4}\,\text{a.u.})$, so that the energy is

$$E(\text{SSA}) = E_0 + \Delta = -0.761292 \quad \text{a.u.}$$
$$= 58.291 \quad \text{eV above the ground state.} \tag{12}$$

Hence, according to this SSA calculation, the energy of the ^2D state is 21 meV below the He $2s2p$ $^3P^o$ state, i.e., it is a Feshbach resonance with respect to this threshold.

By combining the above result with that of Ref. [9] from the CCR calculations and those from measurements [4–6,18–20], we suggest that the energy of He^- $2s2p^2$ ^2D resonance is at 58.295 ± 0.010 eV. We stress that, when the aim for precision is increased, one should be aware that the determination of such energies from measurement depend on the excitation process and the related spectroscopic analysis.

3. The partial widths γ_i and the total width Γ

The results that the energy of the He^- ^2D resonance is 21 meV below that of the He $2s2p$ $^3P^o$ resonance, defines an interesting problem. This has to do with the fact that the width of an N-electron MES (the He^- ^2D resonance) overlaps from below the energy and the width of an $(N-1)$-electron MES (the He $^3P^o$ resonance).

Our ICA results for the partial and total widths are given in Table III. This table also includes the total widths obtained from the close-coupling calculations of Smith *et al.* [47] (25 meV), from the CCR calculations of Bylicki and Nicolaides [9] (49 meV), and from the measurements of Gosselin and Marmet [6] (59 ± 4 meV), and van der Brink [17] (40 ± 10 meV).

The SSA energy dependent golden rule ICA calculations, Eqs. (4)–(5), suggest that no partial width of any of the important channels dominates. It remains to be seen whether interchannel coupling changes this picture drastically.

We now come to the total width. The sum of the ICA partial widths gives $\Gamma = 33$ meV, which is smaller than the widths of Refs. [6,9,17] (Table 3). Our assessment of this fact is given in what follows.

Interchannel coupling and the partial width for two-electron emission, (say about 2–4 meV), both of which were neglected in the ICA computations, would not amount to this difference. A most probable source of inaccuracy in the ICA result is the complete exclusion of the partial widths of the He $2s2p$ $^3P^o$ $\varepsilon p, \varepsilon f$ channels, since these are closed when the definition of the real part of total energy is considered $(E = E_0 + \Delta)$. On the other hand, the overlap of the two states implies that some contribution to the observed width must come from some part of the He $2s2p$ $^3P^o \varepsilon p, \varepsilon f$ continuum. Such a contribution is, in principle, at least taken into account by the CCR calculations of Ref. [9], since the complex eigenvalue of the He^- ^2D resonance is the result of all the interactions and of all the spectral features of the system, including the threshold. Hence, we consider it reasonable, and in harmony with the previously obtained accurate results [9], that the present ICA value to be slightly smaller than the 49 meV computed in Ref. [9].

Although the value calculated in Ref. [9] ought to be the most accurate, given the present results and the experimental values of Gosselin and Marmet [6] (59 ± 4 meV) and of van den Brink [17] (40 ± 10 meV), we recognize that it is not possible yet to accept a precise value for Γ. Our recommendation is that its true value, within the constraints of its dependence on excitation, must lie in the range of 38–55 meV.

VI. SYNOPSIS

Using as examples two triply excited resonance states appearing in the cross-section of electron-He scattering, the He$^-$ $2s^2 2p$ $^2P^o$ at 57.2 eV and the $2s2p^2$ ^2D at 58.3 eV, we examined, critically, aspects of the theory of resonance (autoionizing) states as regards the major interelectronic interactions leading to their formation and quasistability and as regards the quantitative determination of observable properties.

By carrying out a series of small-, as well as of large-scale state-specific calculations with concrete numerical results, we demonstrated how, for these states, wave function localization in an energy local minimum occurs already at the level of the single configuration self-consistent field and how it survives the mixing of additional correlating configurations, including the OCL ones. We conclude that in the model where resonance formation in an atomic negative ion is described by the picture of "*target plus extra electron*," in many cases it will be crucial to account for the response of the target at the orbital level of the major configuration(s), via the use of relaxed and nonorthogonal orbitals.

The analysis and results of this work, together with the ones already in the literature since 1972 (e.g., [1,2,25–30,34,44]) demonstrate that the many-electron, many-channel problem characterizing *inner-hole or multiply excited states* can be solved efficiently and to very good accuracy by applying electronic structure methods that often have to be implemented via NONCI. The first and crucial step is to obtain the state-specific solution of suitable MCHF equations representing the overwhelmingly important strongly mixing configurations, having the structure of closed and, when possible and necessary, of neighboring open channels. A plethora of successful applications show that the main features of these states are revealed accurately once the information about the *self-consistent correlated motion* of the electrons is accounted for. Following the MCHF calculation of the reference wave function, the formation and the electronic structure of excited states in the continuous spectrum can be interpreted and quantified reliably in terms of compact wave functions of the form of Eq. (1).

There are at least three major advantages in this approach to the calculation of resonance states. First, it is not restricted to two- or three-electron systems. The form of Eq. (1) is computable, subject to the localization constraints of the SSA, for arbitrary excited states. Second, the electronic structure characteristics are easily detectable in terms of few configurations. Third, Ψ_0 is usable for the calculation of a variety of properties and phenomena, such as radiationless and radiative widths, relativistic corrections, time-dependent dynamics of decay, photoabsorption cross sections, effects of external ac and dc fields, etc.

By combining the present results, which were obtained according to Eqs. (1)–(7), with those of previous calculations and measurements, we conclude that it is reasonable to recommend the following values for their intrinsic properties: For the He$^-$ $^2P^o$ resonance, $E=57.204\pm0.005\,\text{eV}$ and $\Gamma=68-74\,\text{meV}$. For the ^2D resonance, $E=58.295\pm0.010\,\text{eV}$ and $\Gamma=38-55\,\text{meV}$. The He$^-$ $2s2p^2$ ^2D resonance energy is about 20 meV below that of the He $2s2p$ $^3P^o$ doubly excited state, whose width is 8 meV. Therefore, when the widths are taken into account, these two states overlap.

Finally, the herein reported results of the partial decay widths from energy-dependent golden rule formulas in the ICA are relevant to observation as regards both entrance and exit channels. For the $^2P^o$ state, the largest partial widths were obtained for the $(1s2p\ ^3P^o)\varepsilon s$ and the $(1s2s\ ^1S)\varepsilon p$ channels. If the neglected interchannel coupling does not change this fact drastically, the significance of the $^3P^o$ partial width implies that an additional mode for detecting this resonance indirectly is the synchronized observation of the much slower He $^3P^o-1s2s\ ^3S$ radiative decay. For the ^2D state, there is no apparent dominant decay channel. The channels $2s^2\varepsilon d$, $(1s2p\ ^3P^o)\varepsilon p$, $(1s2s\ ^3S)\varepsilon d$, and $(1s2s\ ^1S)\varepsilon d$ have widths of the same order of magnitude. Finally, it is worth noting that one of the prototypical aspects of the He$^-$ ^2D state is the fact that it overlaps one of its thresholds, the He $2s2p$ $^3P^o$ resonance and this seems to explain the small difference in the total widths calculated by the CCR method [9] and by the present ICA.

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