

# Regular series of doubly excited states inside two-electron continua: Application to $2s^2$ -hole states in neon above the $\text{Ne}^{2+} 1s^2 2s^2 2p^4$ and $1s^2 2s 2p^5$ thresholds

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(Received 20 October 2010; revised manuscript received 7 December 2010; published 3 February 2011)

We report results of many-electron calculations that predict the presence of a regular series of autoionizing doubly excited states (DESS) of  $^1P^o$  symmetry embedded inside one- as well as two-electron continua of neon, in the range of excitation 105.9–121.9 eV above the ground state. The limit of 121.9 eV represents the two-electron ionization threshold (TEIT) labeled by  $\text{Ne}^{2+} 1s^2 2p^6 \ ^1S$ . The wave functions of these unstable states and their properties are computed according to the theoretical framework, which is explained and justified in the text. Their formal structure is  $(\psi_{\text{core}}) \ ^1S \otimes \Phi(\vec{r}_1, \vec{r}_2) \ ^1P^o$ , where both  $\psi_{\text{core}}$  and  $\Phi(\vec{r}_1, \vec{r}_2)$  are correlated wave functions, the latter being represented reasonably accurately by a self-consistently obtained superposition of  $nsnp$  and  $np(n+1)d$  configurations  $n = 3-7$ . By fitting the calculated lowest energies at each value of  $n$ , (five states), an effective hydrogenic formula is obtained, which gives the whole energy spectrum up to the TEIT. The autoionization widths are small and decrease with excitation energy. Oscillator strengths for the excitation of these narrow resonance states by absorption of one photon are also small. Because of their electronic structure, these states are compared to  $^1P^o$  DESS in He, which were found in the 1980s to constitute a regular ladder with wave-function characteristics that tend to those of the so-called Wannier state at threshold. In the present case, the presence of the core and the concomitant interactions do not permit the emergence of such geometrical features.

DOI: [10.1103/PhysRevA.83.022501](https://doi.org/10.1103/PhysRevA.83.022501)

PACS number(s): 31.15.vj, 32.80.Aa, 32.80.Zb

## I. INTRODUCTION

The currently available light sources, such as the synchrotron or the free-electron laser and the anticipated improvements in versions of the near future, provide a spectacular range of frequencies and of intensities for the probing of both the valence and the inner (sub)shells of atoms throughout the Periodic Table and for creating conditions favoring the measurement of a variety of physical effects.

The normally observed and expected type of excitation is the one whereby one electron is excited via absorption of one or more photons. On the other hand, multiple electron excitations are also probable. In this case, given the possibility of using radiation of short wavelengths, an interesting and challenging topic of research is to explore and to understand quantitatively, via the construction and solution of prototypical problems, the possibility of existence of a series of *multiply excited states* (MESs), which, in the independent electron shell model, can be associated with excitation of electrons initially occupying *inner* rather than valence subshells.

A recent experimental example of two-electron excitation from inner subshells is provided by the publication of Argenti *et al.* [1]. These authors presented results of measurements of the triple differential cross sections (TDCSs) for the photodouble ionization of He, Ne, Ar, and Xe from the  $1s^2$ ,  $2s^2$ ,  $3s^2$ , and  $5s^2$  subshells, respectively, at energies of 20 eV above threshold, and successfully demonstrated an approach to the parametrization of the TDCSs. Their analysis of the data included a discussion on the role of angular electron correlation.

Investigations and analyses, such as those of Ref. [1] contribute to the quest for quantitative knowledge and insight

for processes, spectra, and phenomena resulting from the high-energy double-electron excitation of rare gases larger than He, which is the system that is normally examined theoretically for studies of double-electron excitation. Needless to add, such information is even more difficult to obtain quantitatively for  $N$ -electron states whose zero-order description involves open subshells.

In the continuous spectrum of effectively Coulomb attractive potentials in  $N$ -electron systems, there is an infinity of states that can be labeled in zero order as doubly or multiply excited configurations or as superpositions of them. They may or may not correspond to observable resonance states. Of all the possible such MESs, (whose experimental identification and quantitative understanding is still in its infancy), it has been established quantitatively, via the implementation of appropriate theory, that there are classes whose members form *regular series* as a function of the principal quantum number, leading to the corresponding two- [2], three- [3], or four-electron [4] fragmentation thresholds where the electrons exit in unique *symmetrical geometries* with respect to the nuclear position. Specifically, for double ionization, the series tends to a linear geometrical configuration, with the angle of the two vectors tending to  $\vartheta = 180^\circ$  and with  $\langle r_1 \rangle = \langle r_2 \rangle$ , (the Wannier geometry), for triple ionization, the series of  $^4S^o$  symmetry tends to an equilateral triangle [3], and for quadruple ionization, the four-electron ladder of MESs of  $^5S^o$  symmetry in Be tends to a tetrahedral configuration [4]. A concomitant remarkable result is that, in all these cases, the energy spectrum is given accurately by a hydrogenic formula whose effective parameters are obtained by fitting the analytic formula to the energies that are calculated from first principles [2–4].

We stress that the preceding conclusions were quantitative and were obtained by first solving the Schrödinger equation and then using the wave functions and the energies. Alternative studies of MESs, which are keen to descriptive analyses

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and conclusions, start by assuming a classical geometry of the electrons and then obtain results that are related to the corresponding symmetries, such as theoretical rovibronic spectra. For work along these lines, see, for example, Refs. [5,6] for triply excited states and Ref. [7] for quadruply excited states.

In view of the current experimental possibilities, the objective of the theoretical study on which we report here was to explore theoretically and computationally the possibility of the existence of a regular series of doubly excited states (DESS) in the realm of *many-electron systems*, thereby breaking away from the standard cases of the double excitations in the two-electron systems, He or  $H^-$  or positive ions  $Li^+$ , etc.

The reliable treatment of DESs in many-electron atoms (molecules) requires the implementation of a theoretical and computational framework that accounts for a number of important elements of the *many-electron problem* (MEP), such as the opening of various *one-, as well as two-electron continua*, the presence of electronic cores and corresponding valence-core orbital orthogonalities and interaction integrals, and the general relevance of many-electron self-consistent fields and electron correlations.

Specifically, we wanted to explore the possibility of the existence of a regular series of DESs in many-electron atoms that are associated with the following conditions:

- (1) They correspond to one-photon double excitations of *inner subshell* electrons.
- (2) They are embedded inside one- as well as two-electron continua of thresholds different from their own fragmentation threshold.
- (3) The wave functions and the properties of these series of states exhibit some type of distinct regularity as a function of excitation energy below the corresponding two-electron ionization threshold (TEIT), analogous to that of the core-free He-like atoms [2].

For this purpose, we chose to study the possibility that such states, having  $^1P^o$  symmetry, are created in Ne by the one-photon excitation of the pair  $2s^2$  above the thresholds  $Ne^{2+} 1s^2 2s^2 2p^4$  ( $^3P, ^1D, ^1S$ ) and  $1s^2 2s 2p^5$  ( $^3P^o, ^1P^o$ ) and below the two-electron ionization threshold  $1s^2 2p^6 ^1S$ , which is 121.9 eV above the ground state of Ne.

The theoretical and computational frameworks within which the present calculations and analysis were done are explained and justified in Secs. III–V. The results allowed the identification of a novel series of DESs in a polyelectronic system, representing excitations of the  $2s^2$  pair in Ne, which are inside the aforementioned two-electron continua and which lead in a regular way (energywise) to the  $Ne^{2+} 1s^2 2p^6 ^1S$  threshold. (Figure 1 and Sec. V.) The main features of these DESs are as follows:

- (1) Their wave functions are represented mainly by the superposition  $a_1(\text{core} \otimes nsnp) + a_2[(\text{core} \otimes np(n+1)d)] + \dots$  and represent the lowest root at each  $n$  manifold. The core is a correlated wave function having the aforementioned threshold configurations as components. The position of the lowest member is 105.9 eV above  $Ne 1s^2 2s^2 2p^6 ^1S$ .
- (2) As in the coreless cases [2–4], the energy spectrum is given by an effective hydrogenic formula. However, the presence of the open-shell correlated core introduces interactions that destroy the geometrical symmetry of the electron

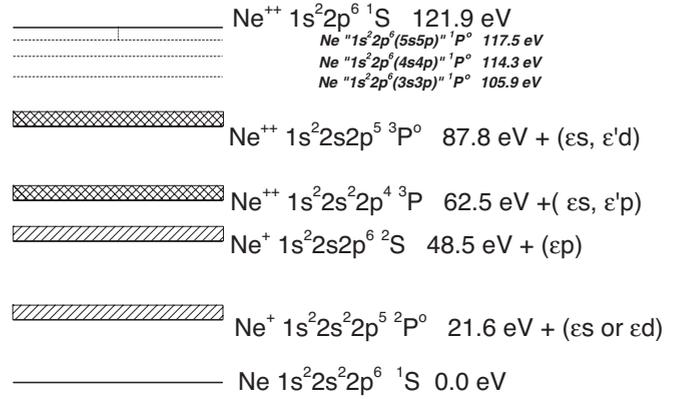


FIG. 1. The part of the Ne spectrum, which is relevant to the  $2s^2$ -hole DESs of  $^1P^o$  symmetry, labeled by  $(1s^2 2p^6) nsnp$  configurations. The energies for the thresholds are experimental (NIST tables). The predicted excitation energies of the DESs are obtained as explained in the text.

densities. Specifically, the angle does open but with a slower rate than in the case of He, and no conclusion as its final value at the TEIT has been drawn. At the same time, the radii do not satisfy the Wannier condition at threshold  $\langle r_1 \rangle = \langle r_2 \rangle$ , a relation that holds in the case of He-like atoms and that emerges quantum mechanically from plots of conditional probability [2].

- (3) The autoionization widths as well as the absorption oscillator strengths from the Ne ground state are very small and decrease as a function of excitation energy.

## II. STATEMENT OF THE PROBLEM

Obviously, in almost all aspects of atomic physics and of quantum chemistry, the case of He does not present the richness of possibilities and the complexities that characterize the spectra and properties of polyelectronic systems.

The theoretical study whose results and conclusions are reported here, was inspired and was guided by the current advances in photon sources, (well-controlled, high-energy, and high-intensity beams), and by the theoretical background that can be found in Refs. [2–4] and in publications cited therein, where the DESs and the MESs are formed in potentials without a multielectron core. These publications have reported numerically accurate results for energies, autoionization total and partial widths, geometries of electron distributions, excitation-dependent trends, and angular correlations, radial correlation, excitation oscillator strengths, new quantum numbers, etc. Indeed, in order to acquire more definitive knowledge as to the behavior of various types of DESs in He, (effective Coulomb attractive potential), as well as in  $H^-$ , the computations have dealt with intrashell as well as intershell DESs up to the hydrogenic threshold  $N = 25$  and have been accompanied by analysis and a brief commentary concerning other approaches [8]. In fact, by being able to obtain and to use wave functions of different degrees of accuracy with regard to the contribution of electron correlation, we explored the degree of validity of the Herrick-Sinanoğlu ( $K, T$ ) quantum numbers [9] and of new ones, namely, the ( $F, T$ ) classification scheme, which was

introduced in 1993 [8]. It was demonstrated that the accurate wave functions of the series of DESs are best represented by the  $(F, T)$  scheme as compared to the  $(K, T)$  one [8]. Furthermore, given the interest in the energy dependence of the double photoionization cross section at  $E = 0$ , related theory and computations with quantitative conclusions were published in Ref. [10].

Given this background, we asked the question whether it is possible to produce, from first principles, quantitative information as to the formation or not of a series of DESs in many-electron atoms having regular properties analogous to those discussed earlier for He, and which could, in principle, be created from the two-electron excitation of inner electrons. Such highly excited unstable DESs, if they can be formed, would exist not only inside one-electron continua below a particular TEIT, but also inside two-electron continua of different TEITs.

If such states exist, of experimental relevance would be questions, such as:

(1) What are the excitation energies? Can they be fit to an analytical formula so as to be able to extrapolate up to the TEIT?

(2) Is there an identifiable symmetric geometry of the two outer electrons as they approach the corresponding TEIT?

(3) What are the magnitudes of the photoabsorption transition probabilities (oscillator strengths) for such one-photon two-electron excitations?

(4) What are the magnitudes of the autoionization widths of these DESs?

Suppose we consider the two-electron excitation from the  $2s^2$  subshell of Ne by absorption of one photon. The feasibility of such a process is documented in Ref. [1]. However, now, instead of the scattering two-electron continuum above the threshold labeled by the  $\text{Ne}^{2+} 1s^2 2p^6 {}^1S$  configuration, we focus on the part of the spectrum below this threshold and, specifically, on the possibility of establishing the existence of a few Ne DESs of  ${}^1P^o$  symmetry that are obviously unstable (resonance states) and have, possibly, properties of regularity as a function of excitation energy toward the  $\text{Ne}^{2+} 1s^2 2p^6 {}^1S$  threshold.

The main difficulties of this problem can be expressed in terms of the following questions (see Fig. 1 for the relevant energy spectrum):

(1) According to the tables of the USA National Institute of Standards and Technology (NIST) (available on the Internet), the  $\text{Ne}^{2+} 1s^2 2p^6 {}^1S$  TEIT is a discrete state located at 121.9 eV above the Ne ground state. Therefore, this discrete level of  $\text{Ne}^{2+}$  is deep into the two-electron continua defined by, at least, five TEITs of  $\text{Ne}^{2+}$ :  $1s^2 2s^2 2p^4$  ( ${}^3P$  at 62.5 eV,  ${}^1D$  at 65.7 eV,  ${}^1S$  at 69.4 eV),  $1s^2 2s 2p^5$  ( ${}^3P^o$  at 87.8 eV,  ${}^1P^o$  at 98.4 eV).

As we know from our previous work since the early 1970s on electron correlation of excited states, the wave function labeled by the  $1s^2 2p^6 {}^1S$  configuration is expected to be highly correlated. Even in zero order, the state is best represented by the three-term superposition of  $[1s^2 2p^6, 1s^2 2s^2 2p^4, (1s^2 2s 2p^4) {}^2D 3d]$  with self-consistent orbitals. This fact, together with the energy spectrum cited previously, means that any Ne DESs of  ${}^1P^o$  symmetry leading to the  $\text{Ne}^{2+} 1s^2 2p^6 {}^1S$  TEIT will have energies above the  $1s^2 2s^2 2p^4$  and

$1s^2 2s 2p^5$  TEITs, while their main components will have the same core structure as these open two-electron channels. So the question arises: How can we computationally establish the existence of  ${}^1P^o$  Ne DESs, which are embedded inside these two-electron continua having the same symmetry?

(2) Indeed, suppose that there are unstable DESs in the energy region of interest. Considering the plethora of possible configurational labels for DESs of  ${}^1P^o$  symmetry, how can we identify and compute valid wave functions for those DESs (if any) that lead in a regular way to the TEIT of  $\text{Ne}^{2+} 1s^2 2p^6 {}^1S$  and how can we determine their geometry?

### III. THEORY AND JUSTIFICATION OF THE STATE-SPECIFIC METHODOLOGY FOR THE COMPUTATION OF THE SERIES OF DESs INSIDE TWO-ELECTRON CONTINUA OF NEON

#### A. Introduction

In order to find the solution to the problem stated earlier and to produce reliable numbers for the intrinsic characteristics of such states, it is necessary to tackle the MEP for open-shell states that, at the start of the treatment of the problem, are hypothesized as being created inside two-electron continua. This implies the possibility of combining the theory of unstable (resonance) states with the polyelectronic structure theory and methods of computation of the electronic structure of excited states in such a way so as to allow the practical reduction of the complexity to physically transparent and computationally tractable levels, without loss of essential accuracy of the relevant answers.

In the following paragraphs, we explain and justify the ingredients of our approach, by first reviewing and commenting on the essential ideas, the computational methods and the results from our earlier publications, which were implemented in this paper. These have been developed according to the following idea: Especially for excited states, it is critically important to utilize *state-specific* forms of the trial wave functions, to analyze the origin and contributions of the different main parts, to represent them by different function spaces, which reflect their different types of contribution to the physics of each problem, and to optimize these functions by suitable procedures. For this reason, the relevant formalisms and methodologies have been named collectively the *state-specific theory* (SST) (e.g., Ref. [11] and references therein).

#### B. Justification of the theoretical framework and of the basics of the methodology implemented in this paper

In our publications on the SST and on the computation of highly excited states that correspond to resonances, it has been emphasized that fundamental to any rigorous and computationally oriented theory is the possibility of obtaining, in a systematic way, the  $N$ -electron square-integrable wave packet, symbolized by  $\psi_0(r_1, \dots, r_N)$ , which represents the localized part of the unstable state and whose energy, (not an exact eigenvalue of the exact Hamiltonian  $H$ ), is determined as a local energy minimum  $E_0 = \langle \psi_0 | H | \psi_0 \rangle$  inside the continuous spectrum (e.g., Ref. [12] and references therein).

One way to see the distinct significance of  $(\Psi_0, E_0)$  is to consider that, on the exact energy of the resonance state  $E_r$ , the  $N$  electron  $\Psi_0$  dominates the character of the resonance state  $\Psi_r(E)$ , through the relation

$$\Psi_r(E) \approx a(E)\Psi_0 \quad \text{for } E \approx E_0, \quad (1)$$

which approximates the exact superposition that includes scattering states [13]. In normal cases of isolated resonances, the energy-dependent complex coefficient  $a(E)$  gives a Lorentzian distribution and satisfies  $\frac{\pi}{2}|a(E_r)|^2 = \tau$ , where  $\tau$  is the mean lifetime corresponding to exponential decay. As the distribution given by  $|a(E)|^2$  tends to a Dirac  $\delta$  function, the resonance state tends to a square integrable discrete state, and  $\tau$  becomes infinite.

In general, the MEP in resonance states of many-electron atoms (molecules) complicates things not only computationally, but also conceptually and formally. For example, the resonance state is in the continuous spectrum, with an infinity of lower states of the same symmetry. In fact, in the case that is studied here, we are looking for resonance states that are embedded in two-electron continua whose thresholds appear as components in the resonance  $\Psi_0$ . Neither the exact resonance eigenfunction nor the localized part  $(\Psi_0, E_0)$  rigorously obey a variational energy minimum principle to all orders. Instead, in a variational calculation subject to appropriate orbital constraints [12,14], what one expects, if the resonance state exists, is a correct convergence to a local energy minimum, secured by the anticipated localization of the state. In addition, there are complications from possible near degeneracies with other resonance states of the same symmetry, and, of course, from the mixing of scattering components.

The key feature in our approach is the argument that, in most cases, wave-function localization is associated with the possibility of finding valid square-integrable solutions of appropriate Hartree-Fock (HF) or, better, of multiconfigurational Hartree-Fock (MCHF) equations for each state of interest. In this way, the computational and interpretational shortcomings, with regard to the MEP, of methods that require the repeated diagonalization of huge Hamiltonian matrices in search of stable roots inside the continuous spectrum, as they were applied in the 1960s to low-lying states of two- or three-electron systems (e.g., Refs. [15–18]) before the introduction of the SST for resonance states [12,14], are bypassed.

Because of the importance of the foregoing argument in this paper, we elaborate by reviewing and commenting on the state-specific computation of  $\Psi_0$ , which was the focus of this paper in the search for the TEIL  $1P^o$  DESs of neon that could possibly result from the double-electron excitation of the  $2s^2$  pair. The use of a basis of explicitly scattering wave functions that are energy normalized is done at the level of frozen core HF theory for the purpose of computing autoionization widths or, if required, photoabsorption cross sections.

The proposal and demonstration in Ref. [14] and in subsequent papers were that, given the correspondence decaying state  $\leftrightarrow$  resonance state, the MEP for the computation of  $\Psi_0$  is best solved by adjusting and adapting formalism and advanced computational methods that were in the process

of being developed in the 1960s (and are still used) for the lowest-lying discrete states. Accordingly, the  $\Psi_0$  for an isolated state [19] is obtained in the form

$$\psi_0 = \Phi_0 + X_{\text{loc}}. \quad (2)$$

$\Phi_0$  stands for the state-specific HF or MCHF solution.  $X_{\text{loc}}$  stands for *localized* correlation and represents those parts of the one-, two-, three-, etc., electron correlation function space that contributes, together with  $\Phi_0$ , to the stability of the state. Since  $\Phi_0$  is the zero-order approximation, the calculation of a valid  $\Psi_0$  hinges on the capacity of first producing a valid state-specific HF or MCHF solution. Once this has been accomplished, useful conclusions may already be drawn at this level and, of course, it becomes possible to proceed with the computation of those parts of  $X_{\text{loc}}$  that are deemed important for the problem under investigation.

Until the beginning of the 1970s, it was not known whether it was legitimate and/or possible to directly solve the HF equations for complicated excited-state structures with open subshells that are in the continuous spectrum. The possibility of state-specific HF computation of even difficult cases of resonance states and the development of theory in the spirit of Eqs. (1) and (2) were first demonstrated in Ref. [14] (see also Ref. [12]) by applying the analytic HF method of Roothaan [20] through the slight modification and judicious use of the computer program written by Roos *et al.* [21]. Since 1972, this approach has been understood better with regard to the computation of both  $\Phi_0$  and  $X_{\text{loc}}$  and has been applied to various problems. One such improvement has to do with the fact that, starting in the mid-1970s, upon the appropriate adaptation of the code published by Froese-Fischer [22], the SST for excited atomic structures has been using the numerical MCHF method for the calculation of  $\Phi_0$ .

### C. The computation of $\Phi_0$ of Eq. (2) via the solution of state-specific MCHF equations

The procedure of solving the MCHF equations for highly excited and heavily mixed states may often provide misleading evidence regarding the question of proper convergence. False convergence is often distinguished because of the appearance of an unlikely orbital with positive energy or of solutions for which the orbital becomes overextended or oscillatory, etc. When proper convergence is absolutely impossible, judgment must be exercised as to whether the resonance exists at all, since there is no localization at this level.

Once the  $\Phi_{\text{MCHF}}$  of Eq. (2) is obtained, (in modern times, this is done systematically for many types of structures), it is possible to compute the main effects of electron correlation and of the multichannel continuum via advanced but practical methods that are based on the use of appropriate function spaces (e.g., Refs. [10–12,19]).

One of the advantages of the state-specific calculation of  $\Phi_{\text{MCHF}}$  is that this wave function accounts in an efficient way for the self-consistently adjusting major correlations that contribute to localization, including a few that incorporate parts of the open-channel continuous spectrum, which we have named the *open-channel-like* (OCL) configurations [23–25]. In the work of this paper, such OCL configurations have been eliminated via appropriate transformations.

State-specific calculations for excited-state structures show that, most often, there is significant dependence of the zero-order orbitals and their electron correlation on symmetry and on spin couplings. The concomitant sensitivity of properties to the level of numerical accuracy at the zero-order approximation constitutes an additional reason for the slow convergence of methods that use a basis set common to various terms of the same configurations, let alone of different configurations. In contradistinction, an SST calculation, by obtaining state-specific zero-order orbitals and corresponding optimized correlation configurations, immediately reduces the magnitude of calculation while considerably increasing its accuracy. Specifically, the calculation of  $X_{\text{loc}}$  involves the proper construction of symmetry-adapted configurations consisting of MCHF and of virtual orbitals and their variational optimization, separately (if needed), and via the minimization into a local minimum of the total energy  $E_0$  using orthonormal or nonorthonormal configuration-interaction techniques [11].

In view of the existing publications to which the reader may refer for extensive discussions and applications of wave functions of the forms (1) and (2), and of their variations, here, we focus briefly on the following three points.

(1) The task of computing  $\Phi_{\text{MCHF}}$  for unstable (resonance) states correctly requires considerable care. For example, it requires stability and high numerical accuracy for large radial distances, the satisfaction of the virial theorem (which is a condition of localization), as a guiding tool for accepting the solution that has converged into a local energy minimum, the attention to the major features of the radial characteristics and of the satisfaction of asymptotically vanishing boundary conditions, the satisfaction of proper orbital orthogonalities, the inclusion of nearly degenerate and OCL configurations, the application of appropriate orbital rotations, etc. Related discussions can be found in Refs. [11,23–25]. These techniques were applied in the present paper when necessary in addition to ones specific to the problem—see Sec. V.

(2) In current times, it may seem that the calculation of highly excited atomic states via the solution of the numerical MCHF scheme is as straightforward as it is for ordinary ground or low-lying discrete excited states in view of the existence of published computer programs, such as the one of Froese-Fischer (Ref. [22] and later versions). This is not so, except for some of the cases of well-localized states, as are Auger states of simple structures, and it certainly was not the case in the early 1970s. For example, in 1978, Froese-Fischer [22], in the preface of her publication, writes: “. . . Since bound states in the continuum interact most strongly with continuum states, a multiconfiguration calculation for such states cannot be performed with this program.” Indeed, for DESs, such as the ones treated here, the determination of proper  $\Phi_{\text{MCHF}}$  wave functions requires careful computation, subject to the criteria mentioned previously.

(3) The strategy of initializing the calculation of autoionizing states with a state-specific MCHF wave function allows the major configurational features of, say, a multiple excited state, to emerge clearly and quantitatively, while the MCHF energy is reasonably close to  $E_0$ . A class of configurations that is very useful and many times absolutely necessary components of  $\Phi_{\text{MCHF}}$  are the OCL type [23–25]. Their presence accounts for a portion of the contribution from the continuum of a

lower-lying threshold, which does not destroy the square integrability of the zeroth-order function. For example, for the triply excited resonance in  $\text{He}^-$  whose label is  $2p^3\ ^2D^o$ , such an OCL configuration is the MCHF  $(2s2p)^3P^o\ ^3d\ ^2D^o$ , which incorporates part of the open channel  $[\text{He}(2s2p)^3P^o + \varepsilon d]^2D^o$ . 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  $\Phi_{\text{MCHF}}$  and of  $\Psi_0$  should exclude them. For example, this is the case of  $\text{He}^- 2s2p^2\ ^2S$ , which interacts with the  $[\text{He}(2s^2) + \varepsilon s]^2S$  continuum. Their effect is then incorporated from principal value integrals over purely scattering function spaces.

#### IV. TREATMENT OF THE ELECTRONIC STRUCTURES OF THE $2s^2$ - HOLE STATES IN NEON

In the present paper, the DESs of interest have the formal structure of  $(\psi_{\text{core}})^1S \otimes \Phi(\vec{r}_1, \vec{r}_2)^1P^o$ , where both  $\psi_{\text{core}}$  and  $\Phi(\vec{r}_1, \vec{r}_2)$  are correlated wave functions, the latter being represented reasonably accurately by a self-consistently obtained superposition of  $nsnp$  and  $np(n+1)d$  configurations  $n=3-7$ .

At first sight, this fact suggests the presence of OCL configurations in the MCHF equations that must be solved, entering as correlation components whose formal structure is the same as that of the open two-electron channels. For example, the  $[1s^22s^22p^4\ ^1S] \otimes \Phi(r_1, r_2)^1P^o$  correlation component has the same structure as the  $[1s^22s^22p^4\ ^1S] \otimes (\varepsilon\ell, \varepsilon'\ell+1)^1P^o$  two-electron continua, where the orbital angular momentum  $\ell=0, 1, \dots$ . On the other hand, the  $[1s^22s2p^43d\ ^1S] \otimes \Phi(r_1, r_2)^1P^o$  correlation component corresponds to closed two-electron channels.

Here, it is computationally convenient to restructure the wave functions so as to have the inner orbital part of the OCL configurations appear as part of the correlation of the  $(N-2)$ -electron core. As a result, the presence of OCL configurations is eliminated from the total wave function. This is achieved as follows.

The zero-order symmetry-adapted MCHF solution for the  $(2s)^0$  double core-hole  $^1S$  state of  $\text{Ne}^{2+}$  is obtained as

$$\Psi_c = b_1(1s^22p^6) + b_2(1s^22s^22p^4) + b_3(1s^22s2p^43d), \quad (3)$$

with  $b_1 = 0.939$ ,  $b_2 = 0.189$ , and  $b_3 = 0.289$ . Note the importance of the  $1s^22s2p^43d$  configuration, which represents the virtual orbital excitation  $s \rightarrow d$ , known to be a significant correlation effect. The presence of this configuration in the core wave function implies that, in the overall calculation, the  $d$  orbitals in the valence wave function  $\Phi(\vec{r}_1, \vec{r}_2)$  must be kept orthogonal to the  $3d$  orbital of the wave function Eq. (2). This is why the MCHF  $d$  orbitals for each shell are written as  $(n+1)d$ .

The energy corresponding to this wave function is  $E_c = -124.1878$  a.u. and has been used to determine the energy difference between each DES and the TEIT.

In the foregoing superposition, the first component is the dominant one. However, there exist two more linear combinations, orthogonal to Eq. (3), where the other components are dominant. They can be considered as approximations to

the core wave functions of the corresponding two-electron continua. Provided that one selects the solutions with the correct core, the DESs will be, to a fair approximation, orthogonal to some important two-electron continua lying energetically below them. Furthermore, a series of states of the same type will converge energetically to the correct value of the core state, which is  $E_c$  in the present case. This selection requires a reorganization of the  $N$ -electron wave functions in a form that makes the part representing the  $(N-2)$ -electron core of Eq. (3) distinct from the excited pair of electrons. We proceed to show how this is done.

Let us start by writing the  $(N-2)$ -electron core  $\Psi_c$  in the form

$$\Psi_c = \sum_i b_i \Psi_i^{(N-2)}. \quad (4)$$

We then label the wave functions of the DESs by a pair of indices. Index  $i$  runs over the  $(N-2)$ -electron configurations of the core, while  $j$  runs over the configurations of the excited electron pair. The total wave function is written as

$$\Psi = \sum_{i,j} c_{ij} \Psi_{ij}^{(N)}. \quad (5)$$

Wave function (5) will now be reorganized as an expansion in terms of the two-electron excitations. This is achieved by a reformulation of the coefficients in a way that the inner core appears as a common factor. Define

$$a_j = \sqrt{\sum_i |c_{ij}|^2} \quad \text{and} \quad \bar{b}_{ij} = \frac{c_{ij}}{a_j}. \quad (6)$$

The wave function of Eq. (5) is now written as

$$\Psi = \sum_j a_j \left\{ \sum_i \bar{b}_{ij} \Psi_{ij}^{(N)} \right\}. \quad (7)$$

The  $N$ -electron wave functions inside the curly brackets resemble the  $(N-2)$ -electron core wave function of Eq. (4) with the basis functions additionally containing a certain pair excitation  $j$ . We define

$$\Psi_j^{(N-2,2)} = \sum_i \bar{b}_{ij} \Psi_{ij}^{(N)}, \quad (8)$$

and select wave functions for which  $\bar{b}_{ij} \approx b_i$  (i.e., those with a structure that resembles  $\Psi_c$ ). Such solutions are expected to exist, as the effect of the excited pair of valence electrons on the core is insignificant for the problem of interest.

In terms of the basis wave functions (8), the total wave function (7) is expanded as

$$\Psi = \sum_j a_j \Psi_j^{(N-2,2)}. \quad (9)$$

Since, by construction,  $\sum_i |\bar{b}_{ij}|^2 = 1$ , while by definition,  $\sum_i |c_{ij}|^2 = 1$ , it also holds that  $\sum_j |a_j|^2 = 1$ . In this way, the initial wave function (5) is reformulated as an expansion in terms of the two-electron excitations in such a way that the combination with the correct core wave function, Eq. (8), is made obvious. As a consequence, these states are orthogonal to the double-electron continua, which correspond to a different linear combination of the  $(N-2)$ -electron core wave function.

Therefore, OCL configurations are actually excluded from the expansion.

The preceding formulation simplifies the result of the calculations by separating out the correlated core and transforming the  $N$ -electron problem to a two-electron one, thus, permitting comparison with the two-electron excitations in He. In order to appreciate the similarities as well as the differences with the case of He, the following discussion is relevant.

Let  $H_c$  be the Hamiltonian matrix that refers to the wave function of the core state. In our approximation, this state is described by three configurations, Eq. (3), and so  $H_c$  is a  $3 \times 3$  matrix. Also, let  $H_v$  be the Hamiltonian matrix that refers to the excited pair of valence electrons. In general, this pair is described by  $M$  configurations, and so  $H_v$  is an  $M \times M$  matrix. If we neglect the core-valence coupling, the zero-order total Hamiltonian  $3M \times 3M$  matrix is the Kronecker sum,

$$H_0 = H_v \oplus H_c \equiv H_v \otimes I_3 + I_M \otimes H_c,$$

where  $I_K$  denotes the  $K \times K$  identity matrix and  $\otimes$  is the Kronecker product [26] of two matrices.

The spectrum of  $H_0$  consists of all pairwise sums of eigenvalues of the two Hamiltonian matrices [26], while the eigenvectors consist of the Kronecker products of the corresponding eigenvectors. One would then have eigenvectors of the form (7), where the  $b$  coefficients are given by Eq. (3), while the  $a$  coefficients are close to the ones obtained for the equivalent He problem of  $^1P^o$  symmetry [2]. For the latter statement to be correct, care must be taken to include in  $H_v$  only the part of the Coulomb attraction that is due to two charges. In other words, full screening must be assumed. The rest of the Coulomb attraction [i.e., the one due to the  $(Z-2)$  charge] is attributed to the core-valence part, where it counterbalances the  $F^0$  integrals that take screening into account.

One might expect that the neglect of the core-valence interaction results in a reasonably accurate zero-order approximation allowing the transfer of the coefficients from the He problem. In fact, this is not the case. The eigenvectors of the Hamiltonian matrix  $H = H_0 + V_{cv}$ , where  $V_{cv}$  is a diagonal  $3M \times 3M$  matrix containing the core-valence couplings, are quite different from those of the He case where such a coupling is absent. The presence of  $V_{cv}$  mainly affects the spectrum of  $H_v$ , so the mixing coefficients of the core part are close to the ones given by Eq. (3). This is expected on physical grounds since the presence of loosely bound valence electrons does not have a significant effect on the core. On the other hand, the behavior of the  $a$  coefficients of Eq. (7) is found to be radically different from the values obtained for the equivalent He problem of  $^1P^o$  symmetry. Specifically, while in the latter case, the dominant coefficient shifts rapidly to configurations containing higher values of orbital angular momenta [2], in the former case, the dominant coefficient is the one of the  $nsnp$  configuration, even for the highest excitation examined  $n = 7$ .

## V. CALCULATIONS AND RESULTS

As explained in Sec. III, the fundamental first step is to determine a reliably converged zero-order wave function of the MCHF type. It turns out that, because of the multiconfigurational wave function of the core, Eq. (3), the construction and convergence of the symmetry-adapted  $N$ -electron wave

functions for the Ne intrashell  $^1P^o$  DESs with high  $n$ , where many angular momentum are, in principle, present, becomes unrealistic and, in fact, unnecessary for the information that we have required. Instead, the DESs MCHF wave functions were obtained by using only the  $nsnp$  and  $np(n+1)d$  components of the excited pair wave functions for  $n = 3, 4, \dots, 7$ . There are six important configurations in all, organized into two groups of three.

Upon transformation of the coefficients leading to Eq. (9), we find  $a_{3s3p} = 0.96$  and  $a_{3p4d} = -0.27$ . These values change little with increasing  $n$ , the first slowly decreasing, and the second slowly increasing. This finding can be compared with the corresponding intrashell states of He, where, already at  $n = 3$ , the mixing coefficients from angular correlation are  $a_{3s3p} = 0.77$  and  $a_{3p3d} = 0.64$ . In fact, as can be found in our previous publication [2], for the coreless case of He, the mixing of intrashell configurations with higher angular momenta increases rapidly as a function of excitation energy, while the coefficient of the  $nsnp$  component diminishes. The obviously significant difference between the two cases is due to the presence of the correlated core in neon.

By subtracting the energies from the MCHF energy of the core threshold state, Eq. (3), we obtained energy differences that were then used in conjunction with the experimental energies of the thresholds of Fig. 1 in order to establish reasonably accurate excitation energies. These are presented in Table I, together with the oscillator strengths from the neon ground state in the length and velocity forms. For the calculation of the oscillator strengths, the wave function of the ground state includes the important correlation configurations for the  $L$  shell [11].

With regard to the Wannier-state characteristics that were found for the He TEIL series [2], these are absent here. We recall that, in the He-like Wannier TEIL states, the MCHF orbital characteristics of radii  $\langle r \rangle_l$  and orbital energies for each  $n$  are very similar, something that is absent in the present DESs of Ne. Furthermore, contrary to the present situation, in He, angular correlation is such that, as  $n$  increases, configurations with higher angular momenta already start dominating for  $n = 5$  [2], something that does not occur in the case that is studied here.

Nevertheless, the energies of these series of DESs do exhibit a regular behavior, with their spectrum given by the hydrogenic formula, as in the case of fragmentation into symmetrical geometries [2–4]. Specifically,

$$E_n = E_c - \frac{(Z - \sigma)^2}{(n - \mu)^2}, \quad (10)$$

with  $Z - \sigma \approx 1.70$  and  $\mu = 0.77$ .

TABLE I. Excitation energies, in eV, and oscillator strengths,  $f_L$  (length form),  $f_V$  (velocity form), from the Ne ground state to the  $^1P^o$  series of DESs created by the excitation of the  $(2s^2)$  electrons.

$n$	$E$ (eV)	$f_L$	$f_V$
3	105.9	$0.35 \times 10^{-4}$	$0.66 \times 10^{-5}$
4	114.3	$0.30 \times 10^{-6}$	$0.18 \times 10^{-6}$
5	117.5	$0.18 \times 10^{-7}$	$0.22 \times 10^{-7}$
6	119.0	$0.27 \times 10^{-8}$	$0.69 \times 10^{-8}$
7	119.8	$0.67 \times 10^{-9}$	$0.20 \times 10^{-8}$

TABLE II. Partial half-widths of the Ne  $^1P^o$  DESs autoionizing states discussed in the text, in a.u..

$N$	" $nsnp$ " $\rightarrow 2s\epsilon p$	" $nsnp$ " $\rightarrow 2p\epsilon s$	" $nsnp$ " $\rightarrow 2p\epsilon d$
3	$1.2 \times 10^{-4}$	$6.9 \times 10^{-8}$	$3.3 \times 10^{-6}$
4	$5.3 \times 10^{-6}$	$3.7 \times 10^{-8}$	$2.1 \times 10^{-7}$
5	$7.8 \times 10^{-7}$	$8.8 \times 10^{-9}$	$3.6 \times 10^{-8}$
6	$2.1 \times 10^{-7}$	$2.4 \times 10^{-9}$	$1.0 \times 10^{-8}$
7	$7.4 \times 10^{-8}$	$1.0 \times 10^{-9}$	$3.7 \times 10^{-9}$

The main channels of decay of the series are the  $\text{Ne}^+ 1s^2 2p^2 2p^5 \epsilon s \ ^1P^o$  and  $\text{Ne}^+ 1s^2 2s^2 2p^5 \epsilon d \ ^1P^o$  through the  $nsnp \rightarrow 2p\epsilon s$  and  $2p\epsilon d$  autoionizing transitions, respectively, as well as the excited-core channel  $\text{Ne}^+[1s^2 2s 2p^6 + 1s^2 2s^2 2p^4 3d] \epsilon p \ ^1P^o$  through the  $nsnp \rightarrow 2p\epsilon s$  autoionizing transition. The one-electron scattering orbitals,  $\epsilon s$ ,  $\epsilon p$ , and  $\epsilon d$ , were computed in the frozen core potential of the corresponding configurations. We observe, from Table II, that it is the  $nsnp \rightarrow 2s\epsilon p$  channel that dominates and essentially determines the resonance width.

The DESs of interest also lie inside the two-electron continua with the  $\text{Ne}^{++}$  core states  $1s^2 2s^2 2p^4$  ( $^3P$ ,  $^1D$ ,  $^1S$ ) and  $1s^2 2s 2p^5$  ( $^3P^o$ ,  $^1P^o$ ). Of these channels, the five ones with symmetries that are different from  $^1S$  do not contribute in a significant way due to orthogonality. The remaining group of channels (i.e., those with the  $^1S$  core) is indeed allowed by symmetry. However, these states are also orthogonal to a very good approximation. This is because, on one hand, they exactly diagonalize the core Hamiltonian, and, on the other hand, the corrections to the core due to the presence of the excited pair of electrons are very small.

## VI. SYNOPSIS AND CONCLUSION

This theoretical and computational paper has focused on the possibility of quantitatively formulating and solving problems of many-electron structures and dynamics that have not been explored thus far, although they are relevant to possible experiments that can probe the deep electronic continuum by using well-characterized radiation of high energy and spectroscopies with high resolution. The essence of these problems is that they are concerned with MESS—in the present case with DESs—in polyelectronic atoms and not just with the DESs of the two-electron systems  $\text{H}^-$ , He,  $\text{Li}^+$ , etc. The latter systems have been studied over many decades in various ways, especially when excitation is low and is far (in relative energy terms) from the TEIT. Presently, on the other hand, if one defines a main theme of atomic physics as the one that aims at the quantitative understanding of MESSs of high energy for polyelectronic atoms across the Periodic Table, then he will find himself in *terra incognita*.

The theoretical framework and justification of the work that was discussed in Secs. II–V, in conjunction with its computational implementation, have allowed the quantitative prediction of the existence and properties of a novel series of unstable DESs inside one- and two-electron continua of a prototypical and experimentally friendly system, namely, the Ne atom.

Specifically, we chose to examine the possibility of computing approximate solutions of the Schrödinger equation that represent DESs of  $^1P^o$  symmetry that are below the  $\text{Ne}^{2+} 1s^2 2p^6 ^1S$  threshold and are embedded inside the two-electron continua of the  $\text{Ne}^{2+} 1s^2 2s^2 2p^4 ^3P$ ,  $^1D$ ,  $^1S$  and  $1s^2 2s 2p^5 ^3P^o$ ,  $^1P^o$  thresholds in addition to one-electron continua. The understanding and proper use of these solutions have allowed the computation of energies and their description by an effective hydrogenic formula leading to the  $\text{Ne}^{2+} 1s^2 2p^6 ^1S$  TEIT [Eq. (10)], of oscillator strengths for the one-photon excitation of the two electrons in the  $2s$  subshell of the  $^1S$  ground state of Ne into these DESs and of the autoionization widths of these DESs, which, because of electronic structure and orthogonality constraints, turn out to be very narrow, despite the fact that they are embedded inside two-electron continua.

With regard to notions of geometry of the electron densities in these DESs as they reach the TEIT, we found that these differ from the analogous ones in coreless He. Now, since we found that the opening of the angle occurs at a slower rate,

it has not been possible to predict with certainty the limiting value. Similarly, the average values of the electron radii are not the same. Therefore, we have concluded that, due mainly to the presence of the core-valence interactions, the series of these  $^1P^o$  DESs does not have the characteristics of the Wannier two-electron ionization ladder that was established for He-like systems [2].

Finally, we comment on the possible relevance of the present results to a recently published experimental-theoretical study of delay in photoemission [27].

That paper investigated the delay in emission between the  $2s$  and the  $2p$  electrons of neon upon the absorption of a photon pulse with the experimental energy of 106 eV and a width at half maximum of 14 eV. The fact that the herein predicted first  $^1P^o$  resonance at 105.9 eV is so close to the photon energy of Ref. [27] has motivated us and a colleague (V. Yakovlev) to explore the possibility that the presence of this resonance influences the overall time delay as measured in Ref. [27]. However, calculations using the approach described in Ref. [27] showed that this is not the case due to the fact that the width of this resonance is very narrow [28].

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