Electronic Structure and the Mechanism of Autoionization for Doubly Excited States

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Apart from pure phenomenology, the rigorous and quantitative study of many-electron autoionizing states presents intriguing questions as regards their structure and dynamics. In this paper we present an analysis of such states within a state specific theory with application to five low-lying doubly excited states (DES) of He. The zeroth order description is multiconfigurational and is obtained numerically at the MCHF level. In this way, major radial and angular correlations are accounted for accurately, and reliable predictions can be made without the requirement of large computations. The additional localized correlation is obtained by optimizing variationally analytic virtual orbitals. Core orbitals corresponding to the open channels are projected out of the MCHF solutions, as well as out of the correlation functions. The asymptotic correlation, which gives rise to autoionization, is computed from a multichannel reaction matrix approach. It is shown that when calculating the width, the Rydberg series should not be part of the localized correlation if the frozen-core Hartree-Fock scheme is used for the generation of bound and scattering orbitals of each channel. Our calculations of the width of the first three \(^1S\) DES of He include the effects of coupling of resonances via the continuum. The wavefunctions for the \(2s^2\) and \(2p^2\) \(^1S\) DES, together with a Hartree-Fock scattering orbital in the field of He\(^+\) \(1s\) are employed for the calculation of two quantities introduced by Rehmus, Ezra and Berry to the study of doubly excited states of He. The “conditional probability density", \(\rho\), and the “differential transition amplitude", \(D\). As regards \(\rho\), our approach yields results which agree with those of Rehmus et al. However, as regards \(D\) our results contradict their conclusions. In particular, we are forced to disagree with their proposal about the “generalized \(S_{\chi} - 2\) mechanism" for atomic autoionization. Instead, we propose a mechanism which is based on the interelectronic repulsion and the heavy overlap of bound and scattering orbitals in small regions of space. This mechanism is in harmony with the generally observed slower rates of autoionization for triplets as compared to those of singlet states of the same orbital angular momentum.

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I. Introduction

Resonances and the phenomenon of autoionization present interesting challenges to the quantum theory of the structure and dynamics of many-electron systems. Their rigorous and quantitative understanding requires the application of many-electron approaches to the discrete as well as to the continuous spectrum. In this context, the important questions are related to the appropriate choice and manipulation of bound and scattering wave-functions which enter the calculation of the intrinsic properties of autoionizing states, the energy and the width.

In recent years, the dimension of graphical display has been added to the analysis of correlated wave-functions of DES in two-electron atoms [1–6].
Rehmus, Ezra and Berry [1–5] computed and plotted two quantities for He DES:

a) The “conditional probability density”, \( \rho \)

and

b) The “differential transition amplitude”, \( D \).

The first was employed mainly in drawing conclusions about the nature of certain DES from the point of view of the “rotor-vibrator” model of DES introduced by Kellman and Herrick [7, 8]. It displays the probability density of finding the second electron once the position of the first has been fixed for square integrable functions. The same concept has been used for the display of pair correlation functions of simple atoms [9, 10].

The second quantity involves the behaviour of the integrand of the autoionization matrix element at various points of coordinate space. Rehmus and Berry introduced it [4, 5] with the aim of gaining insight into the contribution of the various terms of the coupling operator and of the relative motion of the two electrons to the probability of autoionization.

The method for obtaining the DES wave-functions was the stabilization of roots of large diagonalized matrices obtained in terms of Hylleraas or Sturmian basis sets.

The purpose of this paper is twofold:

First, to apply a state-specific theory of autoionizing states [11–15] which emphasizes the self-consistent calculation of multiconfigurational zeroth order wave-functions of inner hole excited states (IJES) or of DES. Given the previous interest in them, we have studied the first three DES of He of \( ^1S \) symmetry and the lowest DES of \( ^3P^0 \) and \( ^1P^0 \) symmetries. Energies as well as widths are obtained and are compared with available experimental and theoretical values.

Second, to present results on the quantities \( \rho \) and \( D \) obtained using these wave-functions and the HF continuum orbitals, and to compare them with those of [1–5]. We have found agreement as regards the conditional probability density and the widths, but disagreement as regards the differential transition amplitude and the conclusions drawn from it.

II. Theory of Wave-Functions and Widths of Many-Electron Autoionizing States

In most computational theories of excited states, the function spaces are chosen from large common basis sets-regardless of the formalism used [e.g. 1, 6, 16, 23] Although the size and flexibility of such basis sets may often be sufficient, especially when dealing with two-electron atoms, it is possible for computational as well as conceptual limitations to intrude.

In a number of papers on autoionization [11–15, 24–26] it has been shown that for doubly excited states (DES) as well as inner hole excited states (IHES), Hartree-Fock (HF) as well as Multi-Configurational Hartree-Fock (MCHF) theory applies and the computations can be made to converge for the state of interest. The physical content of orbital occupancy, proper number of radial nodes and the satisfaction of the virial theorem have constituted the basic elements of justification for the adoption of this theory for obtaining bound wave-functions of IHES and DES in zeroth order. Given this fact, a state-specific [27] theory of electronic structure has been developed in terms of real or complex coordinates [11–15], with formal elements analogous to those of the many-body theory of bound states but with special attention to the peculiarities and difficulties of the strongly correlated excited states and the physical significance of the open channels.

The gain of this state-specific theory over the conventional approaches (i.e. very large basis sets and repeated diagonalization, or use of projection operators applicable only to two-electron systems) is manifold:

Reliable applications to N-electron IHES and DES (and not only to two-electron atoms) is straight-forward. Relaxation as well as the most important radial and angular correlation are incorporated consistently and accurately via the solution of MCHF equations [28, 29]. For example, in Ref.12 it was demonstrated that for the \( ^1\text{He}^+ \, ^1S \times 2 \times 2p \times 2p^0 \) resonance, a two-term MCHF calculation already yields a better energy than the calculations of Refs. 30 and 31 where 54 and 40 configurations were employed respectively.

Similar results can be found elsewhere [24, 27] (see also, Table 1). More recently we have applied this approach to the calculation of a theoretically established DES class of high-lying (up to \( n=10 \)) which are related to the two-electron threshold ionization process [32].

Furthermore, systematics have been developed as to types of correlation effects which alter drastically the single configurational description [11, 33, 37] or as to those electron-electron interactions which contribute to the stability of the autoionizing state and those which contribute to its decay [11–14]. Essential to this work was the justification of the variational calculation of the stabilizing correlation functions for N-electron \( (N>2) \) IHES and DES, which was first presented and implemented in Ref.11 via suitable orthogonality constraints and orbital projection operators. (The MCHF orbitals are made
### Table 1. Energies of He doubly excited states obtained by a variety of many-electron approaches. They are given in eV above the ground state \( \Phi(He) = -2.903724 \) a.u. \( 1 \) a.u. = 27.206 eV. For the zeroth order configurational assignment, see the Fermi-Sea vectors of the text.

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(a) Bhatia and Temkin (Ref. 20): Projected variational with Hylleraas basis
(b) O'Malley and Gelmont (Ref. 16): Projected variational with STO basis
(c) Ezra and Berry (Ref. 2): Stabilization with Surnman basis
(d) Burke and Taylor (Ref. 17): Cluster coupling with correlation
(e) Connelly and Lipsky (Ref. 22): Truncated diagonalization with hydrogenic basis
(f) Ho (Ref. 21): Complex coordinate rotation with Hylleraas basis
(g) Holstein and Mittleman (Ref. 18): Stabilization with Surnman basis
(h) Ramaker and Schrader (Ref. 26): Multichannel CI with Hartree-Fock basis sets
(i) This work (Projected Fermi-Sea MCHF, see text)
(j) This work (Projected Fermi-Sea MCHF + variational correlation). The size of these state-specific functions is smaller than that of the other methods.
(k) Madden and Codling (Ref. 59): Photoabsorption experiment
(l) Hicks and Comer (Ref. 60): Scattering experiment. The \( ^3 \)P 0 energy is made equal to that of \( ^3 \)S 0.

Orthogonal to core orbitals of lower thresholds as well.

**11a. The Fermi-Sea Zeroth Order Approximation for DES Quantitative and Qualitative Predictions**

Because of near-degeneracies, the single configurational description (SCD) of DES in terms of the ordinary symmetry orbitals is not accurate. This fact has led to developments based on new symmetry concepts and approximate constants of motion which offer new, high purity SCD of DES in terms of new quantum numbers [23, 38, 6]. The radial characteristics of these zeroth order functions are expressed in terms of hydrogenic basis sets. Similarly, collective coordinates — the so-called hyperspherical coordinates — have been employed, leading to new modes of qualitative description of DES [6, 39, 40].

Our approach is based on the self-consistent computation of a multiconfigurational zeroth order vector expanded in terms of the strongly mixing Fermi-Sea [32–34, 12, 13] configurations. In this way, the concerted motion of the electrons is computed optimally, taking into account the important radial and angular correlations.

It might be suggested that it is more elegant to have a zeroth order representation of the state of interest in terms of one rather than many configurations. Nevertheless, it appears to us that the important element in the zeroth order choice of any many-body problem is that it is done consistently and that its physical content is of high quality. Furthermore, in our specific situation, the multiconfigurational Hartree-Fock (MCHF) vector constitutes a manageable zeroth order function which can be used as input for a complete computation of electron correlation.

In symbolic notation, we write the subshell cluster expansion of a many-electron wavefunction in the continuous spectrum in the vicinity of an isolated resonance as:

\[ \Psi(E) = \Phi_{FS} + \Phi_{FS}^{-1} \sigma(E) + \Phi_{FS}^{-2} \pi(E) + \Phi_{FS}^{-3} \tau(E) + \ldots \]

(1)

\( \sigma(E), \pi(E), \tau(E) \) etc. are single, pair, triple etc. correlation functions corresponding to closed as well as to open channels. Aspects of their calculation are presented in the next section.

\( \Phi_{FS} \) is the Fermi-Sea (FS) zeroth order function obtained in general at the MCHF level. It is a bound, localized function which, when solved accurately, satisfies the virial theorem very well. Furthermore, the numerical MCHF representation of \( \Phi_{FS} \) guarantees the exclusion of orbitals (and states) with different number of nodes and energy, while by imposing orthogonality to selected core orbitals during the solution of the coupled integrodifferential equations, possible admixtures from lower configurations are eliminated [11].
The concept of the Fermi-Sea zeroth order vector [27, 33, 34] implies the identification of strongly mixing configurations and the determination of their optimized one-electron radial functions. For ground or low-lying bound states, this task is computationally and conceptually easier than it is for DES of neutral systems. In DES, the near-degeneracies are enhanced, the strength of off-diagonal matrix elements are hard to predict consistently and the known spectra are few and not well-identified. Thus, the a priori choice of certain configurations, e.g. ns^2 \rightarrow np^2 for 1S or npnd \rightarrow nsmsf for 3^1P^0, must be accompanied by trial variational calculations with larger matrices from which knowledge can be gained as to the importance or not of additional configurations in completing the Fermi-Sea or in establishing the correct ordering of the main roots. Such calculations are based essentially on experience and on a priori analysis of the spectral features.

The FS-MCHF zeroth order wave-functions which are given below were obtained after a series of calculations indicated that their choice constitutes a very good zeroth order description of the corresponding D+S: Table 1 – where comparison is made with much larger-size computations and with experiment demonstrates again [12, 24, 27] that very small but state-specific zeroth order functions can yield energies which are very close to the accurate ones.

Of the three 1S DES of He, the lowest FS-MCHF is, as expected, the simplest:

\[1\ 1^1S_{\text{FS-MCHF}} = 0.8586(2s^2) - 0.5126(2p^2).\]

Only intrashell (n=2) configurations contribute. However, for the next two 1S DES the contributing configurations are not limited to the intrashell type:

\[2\ 1^1S_{\text{FS-MCHF}} = 0.7432(2p^2) - 0.5881(2s^2) + 0.1907(3s^2) - 0.1838(3d^2) - 0.1344(3p^2) - 0.1089(2s\ 3s) - 0.0402(2p\ 3p).\]

\[3\ 1^1S_{\text{FS-MCHF}} = 0.718(2s^3) + 0.621(2p\ 3p) + 0.233(2s^2) - 0.171(2s\ 4s) - 0.076(2p^2) + 0.078(3d^2) - 0.048(3p^2) - 0.025(3s^2).\]

Convergence of the above solutions has been difficult. A combination of numerical MCHF with analytic MCHF was employed. The presence of the configurations with n=3 turned out to be absolutely necessary for convergence and correct root ordering even though their coefficients are, in most cases, rather small. Such situations are expected to appear in a large number of cases with near-degeneracies, strong off-diagonal matrix elements and root crossings.

For the lowest 3^1P^0 and 1^1P^0 DES, the FS-MCHF functions are

\[1\ 3^1P^0_{\text{FS-MCHF}} = 0.993(2s\ 2p) + 0.119(2p\ 3d)\]
\[1\ 1^1P^0_{\text{FS-MCHF}} = 0.949(2s\ 2p) - 0.314(2p\ 3d).\]

The value of the state-specific Fermi-Sea zeroth order vectors goes beyond the possibility for efficient quantitative predictions that they offer. They can also form the input for analyses of DES in the spirit of those of Rehmus, Ezra and Berry [1,3], which however, required particular plots from extensive calculations.

For example, consider a DES state of 1^1P^0 symmetry. It consists of configurations with (l,l+1) orbital structure and symmetric spatial part. Each such configuration may then be shown to possess a node in the probability density distribution at r_1 = -r_2 and a maximum at r_1 = 0. If more than one configurations mix strongly in the state of interest, the total density will still retain the node at r_1 = -r_2 but the rest of the angular behavior will depend on the relative contributions, which may add either constructively or destructively. An example of destructive mixing is offered by the lowest (2s2p^2) 1^1P^0 state in helium. For this DES, density is excluded both from r_1 = r_2 (0°) and r_1 = -r_2 (180°) and is accumulated around 90°. Consider the MCHF vector shown above. When we calculate it along the isoelectronic sequence we find that the mixing of 2p 3d into the 2s2p configuration is reduced considerably – in accordance with what is expected from the hydrogenic picture. At Z = 7 the coefficient of 2s2p is already 0.995 while that of 2p 3d is 0.100. Thus, it is clear that this 1^1P^0 state becomes purely antirotor-like, as has already been confirmed by computation (see Fig. 3, and the paper by Ezra and Berry [2]).

As another example, let us consider the lowest (2s2p^2) 3^1P^0 state. The mixing here is smaller than in 1^1P^0 and, as with the case of 1^1P^0 it diminishes as a function of Z. At Z = 7, the coefficient of the 2p 3d configuration is 0.034, almost negligible, while that of 2s2p is 0.999. Other correlation effects cannot alter significantly this high level of purity. Each 3^1P^0 configuration has a node (Fermi hole) at r_1 = r_2 and accumulates density at r_1 = -r_2. Since the 2s2p configuration is in essence dominant already in He(Z = 2), we may predict a rotor behavior for the whole series with Z ≥ 2. This is true, as we conclude from Fig. 4 and the paper of Ezra and Berry [2].
The cases of states with intrashell Fermi-Sea structure are somewhat different. The mixing there increases with increasing Z, according to the hydrogenic near degeneracies. For the two lowest $1^S$ resonances, the mixing is strong already in He. These states ($2s^2$ and $2p^2$) consist of orbitals of equal $\ell$s. There are no common characteristics among these configurations (i.e., no coinciding nodes or maxima). Therefore, although the shape of each configuration may be determined in a trivial way by application of the addition theorem, the spatial characteristics of the wavefunction cannot be easily anticipated in general.

The gross understanding of the other low-lying DES can be carried out in a similar, straightforward manner.

Thus, the state-specific approach to the DES problem (and the use of the MCHF-implemented Fermi-Sea concept) is seen to offer easy means of analysis already at the zeroth order level. Furthermore, the Fermi-Sea zeroth order functions yield good energies (Refs. 11, 12, 24, and Table 1) and, as this work shows, the conditional probability densities are close to the accurate ones.

IIb. Localized and Asymptotic Correlation Functions

The functions $\sigma(E), \pi(E), \tau(E)$ are symmetry adapted correlation functions, corresponding to single, pair, triple etc. virtual as well as real (i.e., autoionizing) excitations. We write [13, 15]:

$$\sigma(E) = \sigma_{loc} + \sigma_{as}(E)$$

$$\pi(E) = \pi_{loc} + \pi_{as}(E)$$

and similarly for the larger clusters. (It has been established that for ground or low-lying bound states of small atoms $\pi$ is unimportant. However, for highly excited negative ion states, it was predicted [11a] and found [27, 41] to be relatively more important).

The orthogonal separation into $\text{loc}$ (i.e., localized) and $\text{as}$ (i.e., asymptotic) correlation signifies the fact that, beyond the zeroth order bound vector, part of the interelectronic interaction contributes to the stability of the system and part to its decay. Thus, the asymptotic correlation functions are energy dependent because they contain the open channels.

For closed channel resonances, (the so-called Feshbach resonances), $\pi_{as}(E)$ is zero. This term is non-zero and physically significant in the cases of open channel resonances, the so-called shape resonances. For example, consider the configuration $1s2p^4{}^4P$. It was shown in Refs. 41, 42 that in He$^+$, contrary to previous belief, it corresponds to a shape resonance which contributes to the absorption or emission spectrum significantly just above the $1\text{He}1s2p^3{}^1P_0$ threshold. There, the single excitation out of the $2p$ subshell gives rise to $\sigma_{as}(E)$ (i.e., free electron orbital of $p$ symmetry) which, due to its overlap with the HF $2p$ orbital of the $1s2p^4{}^4P$ configuration, causes the finite width of this state. We note that, because of symmetry, for the $1s2p^4{}^4P$ He$^+$ resonance, $\pi_{as}(E)$ is zero. On the contrary, for the $1s2p^4{}^2D$ resonance, $\pi_{as}(E)$ represents the $1s\text{He}$ open channel which mixes with $1s2p^4{}^2D$.

The $\pi(E)$ functions are the most significant contributors to the real as well as to the imaginary parts of the resonance energy for the majority of autoionizing states. The $\pi_{loc}$ can be expressed as a sum of Rydberg series plus an unknown function $\tilde{\pi}(r_1, r_2)$:

$$\pi_{loc} = \sum_k (n|k\ell) + \tilde{\pi}$$

where $(n|k\ell)$ is a Hartree-Fock orbital corresponding to the hole in the $(n|k\ell)$ subshell.

In principle, the sum in [3] could also include contributions from the continuum, provided a principal value integral around $E_0$ is excluded, having the form:

$$P.V. \int_{E_0 - \infty}^{E_0 + \infty} dE \phi_i(E') V(E') \frac{1}{E_0 - E'}$$

where $V(E)$ is the interaction between the occupied pair of HF orbitals and the continuum $|n\ell\rangle \phi_i(E')$. $R$ is a small number whose function is in fact to exclude the infinite terms from $\pi_{loc}$.

The finite terms are of the form $\int_{E_0 - R}^{E_0 + R} dE \left| V(E') \right|^2 \frac{1}{E_0 - E}$ and $\int_{-\infty}^{E_0 - R} dE \left| V(E') \right|^2$.

However, the arbitrariness of $R$ does not allow a consistent and general definition of $\Psi_0$ unless the whole continuum is excluded from $\pi_{loc}$.

The unknown $\tilde{\pi}$ can be expanded in terms of basis sets and optimized variationally subject to the orthogonality constraints [11]

$$\langle \tilde{\pi}(r_1, r_2) | n\ell \rangle_{r_1, r_2} = 0.$$  (3a)

The HF $|n\ell\rangle$ orbital is chosen for each state of interest. As stated in Ref. 11a, p. 2088, condition (3a) is equivalent to the use of orbital projection operators $q = |n\ell\rangle \langle n\ell|$ for many-electron systems, which are necessary to establish variational upper bounds valid to second order in perturbation theory.
The sum of $\Phi_{\pm}$ and the terms containing the localized correlation clusters constitute $\Psi_0$.

**IIc. The Choice of the Initial and Final State Wave-Functions for the Calculation of Autoionization Widths**

The calculation of autoionization rates by any method requires the consideration of the appropriate square integrable and scattering function spaces. This applies to the familiar first order expression for energy independent isolated resonances

$$I^* = 2\pi |\langle \psi | H - E_0 | f(E_0) \rangle|^2$$  \hspace{1cm} (4)

where $\psi$ and $f$ are the initial and final state wavefunctions which, in general, need not be orthonormal [11-14, 43-47]. It also applies to the other methods which do not use Eq. 4 [14, 17, 21].

Regardless of the method used, the important question involves the choice and optimization of these function spaces. As regards the final state, we have concluded – as anticipated in Ref. IIa – that for single as well as for multichannel problems, the term dependent frozen core Hartree-Fock scheme [48] offers good basis sets of scattering orbitals. These are obtained in the Hartree-Fock field of the main $(N-1)$ $(N$ is the number of electrons) configuration of the ionic core and are coupled to the core which is correlated in a state specific manner [33]. The problem of interchannel coupling and of the mixing of valence and correlation vectors has been solved by implementing a reaction matrix, configuration interaction in the continuum (CIC) approach [15, 26].

As regards the initial state square integrable function, interesting questions arise from the representation and use of $\pi_{\text{noc}}$ of (3). This subshell pair correlation function contains the Rydberg series of the corresponding channel. The orthogonal part $\tilde{\pi}$ represents doubly excited correlation vectors with variationally optimized virtual orbitals.

The importance of the series depends on the type of state and on the property under examination. For example, for the DES of He, the series mixing depends on $K-L$ shell interaction matrix elements which are small. Therefore, their effect on $\Psi_0$ and the energy is small. We note that in the variational projection operator treatment [16, 20] the series are excluded from the QHO space but their effect on the total energy can be included via the computation of the energy shift, $\lambda$, as a sum over the series. On the other hand, in the truncated diagonalization calculations of Holstein and Lipsky and Russek [49] they are included. In fact, the latter authors discussed extensively the questions of choice of function spaces of lower states and continuum components and of projection operators for two-electron autoionizing states.

For larger systems, the importance of the series may increase significantly in two cases.

1) If the resonance is close to threshold (For example, the Be $1s^2 2p^3 3S$ state [50, 51]) and

2) If the two electron rearrangement involves neighboring shells and the correlation is of the SEOS type [33, 36, 14]. These cases are abundant throughout the periodic table. Strong valence (autoionizing)-Rydberg mixings exist in molecules as well.

Thus, we have posed the following questions about autoionizing states: How should the Rydberg series be treated? Should they be included in $\Psi_0$ when evaluating diagonal or off-diagonal matrix elements for various properties? (In fact, the last question arises in valence-Rydberg interactions even when the valence configuration represents a bound state).

In earlier work [11, 50], which did not include the accurate calculation of widths, we approximated the single electron channel (Rydbergs plus continuum) by a few Slater type orbitals. The object was to include in $\Psi_0$ the main characteristics of this function space, which could in principle affect transition matrix elements. Apart from the knowledge that near degeneracies between the valence and the pseudoccontinuum configurations should be avoided, the reliability and systematics (if any) of such an approximation are not known.

In our recent calculations of widths [12, 13, 24] this question was not important (from the practical point of view) since the valence-Rydberg mixing was very small. Only the lowest member was included which has the most non-Rydberg character.

Here we show that the frozen-core Hartree-Fock scheme is a convenient method for choosing Rydberg and scattering orbitals since it has the property of simplifying the computation of widths with respect to the questions posed earlier.

We proceed by first demonstrating the issue for a reasonably complex, two channel autoionizing state, the $F 1s^2 2s 2p^6 3S$. This configuration has been predicted [52] to give rise to a strong resonance in the photoabsorption cross-section of $F$, about 22 eV above the ground state, with a width of $\Gamma = 3.1$ eV and a Fano parameter $q = 2.2$. (Interchannel coupling was neglected).

According to theory, first a HF function is computed for the $1s^2 2s 2p^6 3S$ configuration. It is obvious that autoionization occurs because of electron
correlation in the $2p$ shell. We have:
\begin{equation}
\pi(2p^2) = \pi_{\text{loc}}(2p^2) + \pi_{\text{ex}}(2p^2).
\end{equation}
(9)

$\pi_{\text{ex}}(2p^2)$ corresponds to the open channels $2s\text{es}$ and $2s\text{ed}$. $\pi_{\text{loc}}$ is expanded as:
\begin{align}
\pi_{\text{loc}}(D) &= \sum_{n=3}^{7} [2s^2 2p^4 4D] nd + \hat{n}(D) \\
\pi_{\text{loc}}(S) &= \sum_{n=3}^{7} [2s^2 2p^4 4S] ns + \hat{n}(S).
\end{align}
(10a) (10b)

Of these, the lowest Rydberg SEOS configuration, $1s^2 2s^2 2p^4 3d$, has the largest mixing with $1s^2 2s 2p^6$. The variational $\pi$ are orthogonalized to the $2s$ orbital of the core:
\begin{equation}
\langle \hat{n} | 2s \rangle_{rer=2} = 0.
\end{equation}
(11)

The $2s$ and $2p$ orbitals are state-specific. For example, the HF $2s$ orbitals of the $1s^2 2s^2 2p^6 2S$ configuration is not the same as the HF $2s$ orbitals of the $1s^2 2s^2 2p^6 nd$, $cd$, $ns$, $es$ configurations, designated by $2s$, so that
\begin{equation}
\langle 2s | 2s \rangle \neq 1.
\end{equation}
(12a)

Also, in the frozen core HF scheme
\begin{align}
\langle n| \hat{n} | 2s \rangle &= 0, \quad l = 0, 2 \\
\langle 2s^2 2p^4 n| \hat{n} | 2s^2 2p^4 2e \rangle &= 0, \quad l = 0, 2 \\
\langle 2s^2 2p^4 n| H | 2s^2 2p^6 \rangle &= 0 \\
\langle 2s^2 2p^4 n| H | 2s^2 2p^6 \rangle &= 0.
\end{align}
(12b) (12c) (12d) (12e)

The interesting question is related to $12e$. These matrix elements not only affect the coefficients of $\phi_{1s}$ and of $\hat{n}$ but also, one could argue that as more Rydberg configurations are included, $\Psi_0$ could become extremely extended in position space and the notion of localization and separation from the asymptotic region diluted accordingly. This last ambiguity is lifted since, as $a$ small, the Rydberg functions cease to overlap the inner region and their contribution to (12e) tends to zero. Here we note that one may think that if a valence configuration does not interact substantially with the Rydberg series it will not interact with the continuum either. This is not necessarily true since the size of the scattering orbitals of the channel where a Rydberg series belongs is larger in the inner region due to the different normalization.

Equations (12) thus lead to the realistic model of a correlated discrete function $U_0$ embedded in the continuum and interacting with a Rydberg series $R_a$ below it and with the scattering states $U(E)$ whose channel orbitals are obtained by the HF scheme. This model is defined by
\begin{align}
\langle U_0 | H | U_0 \rangle &= \epsilon_0, \\
\langle U_0 | H | R_a \rangle &= V_a \\
\langle R_a | U(E) \rangle &= V_a, \\
\langle U(E) | H | U(E) \rangle &= E \delta(E - E') \\
\langle R_a | H | U(E) \rangle &= \langle R_a | U(E) \rangle = 0.
\end{align}
(13a) (13b) (13c) (13d)

The complete solution of this problem is given by Fano's theory [53] and involves the determination of the expansion coefficients of the exact wave-function, $\Psi(E)$.
\begin{equation}
\Psi(E) = U_0 \sum_a Q_a R_a + \int dE' h_{E'} U(E')
\end{equation}
(14)

and the phase shift $\delta$ (and corresponding width) derived from them.

Defining the interaction matrix $F_{mn}(E)$ by
\begin{align}
F_{00}(E) &= P \cdot \int dE' \left| \frac{V}{E - E'} \right|^2 \equiv F(E) \\
F_{ij}(E) &= \delta_{ij} \delta_{a_i} F(E) \quad i, j = n \quad \text{for} \quad U_n \\
F_{ij}(E) &= \delta_{ij} \delta_{a_i} F(E) \quad i, j = n \quad \text{for} \quad R_n
\end{align}
(15a) (15b)

the problem of the CIC is reduced to the diagonalization of the matrix
\begin{equation}
H_{mn} + F_{mn}(E) = \begin{pmatrix}
\epsilon_0 + F(E) & V_1 & V_2 & \cdots & V_k \\
V_1 & \epsilon_3 & & & \\
& V_2 & \epsilon_3 & & \\
& & \ddots & \ddots & \\
& & & V_k & \epsilon_a
\end{pmatrix}
\end{equation}
(16)

whose straightforward solution yields for the phase shift
\begin{equation}
\tan \delta = -\pi |V'|^2 \left[ E - \epsilon_0 - F(E) - \sum_a \frac{|V_a|^2}{E - \epsilon_a} \right]^{-1}.
\end{equation}
(17)

Equation (17) is the same as the one obtained from Fano's [53] case of one discrete-one continuum (his equation (15)), where the discrete state is represented by $U_0$, and the continuum by the sum of scattering plus Rydberg series.

This result implies practically that in computing (4) the initial state wave-function should be obtained in the absence of the Rydberg series if the relations 13 apply. Naturally, due to (13d) and the first order character of (4), the $R_n$ do not enter in the calculation of the final state wave-function either. On the other hand, lower lying valence as well as Rydberg-like configurations which are not eigenfunctions of a frozen core Hartree-Fock potential should be included in $\Psi_0$. For example, such is the case of the $1s^2$. 
1s2s and 2s2 configurations which enter in the calculation of the 2p2 1S square integrable $\Psi_0$.

The widths from our calculations, using (4), are given in Table 2 and are compared to available experimental values. The size of our state-specific $\Psi_0$ functions is 32 terms (up to g orbitals) for the three $^1S$ states and 18 terms (up to f orbitals) for the $3p^5$, $3p^6$ states. Larger expansions could be created. However, given the good convergence properties of the state specific theory [12, 13, 27] - see Table 1 this was considered unnecessary.

### II.d. Higher-Order Effects on the Widths of the 1S States Due to Coupling via the Continuum

The present theory of autoionization allows for the systematic calculation of partial and total widths using either real or complex coordinates [11 15]). In the case of a single channel, isolated resonance, one needs only the initial state square-integrable wavefunction $\Psi_0$ and a continuum function consisting of a correlated core and a Hartree-Fock scattering orbital. However, in general, there are two types of extensions which are necessitated by the physics of autoionization and which require significant expansion of the isolated resonance theory. The first involves the consideration and accurate calculation of a multichannel continuum and the second involves the coupling of the initial state wave-function $\Psi_0$ to square-integrable correlated wave-functions of other resonances via the continuum. Komninos and Nicolaides [15] have developed and implemented numerically a general configuration-interaction reaction-matrix theory which applies to the continuous as well as to the discrete spectrum [54]. The theory has already been applied, approximately or exactly, to a case of bound-bound coupling via the continuum [12], to a case of a multichannel continuum [26] and to the case of Rydberg series of resonances Quantum Defect Theory and photoionization [15].

According to the above, the use of the first order formula for each resonance (4) implies the neglect of the effect of interactions among the various resonances via the continuum.

In order to determine the size of such higher order effects, we have followed the procedure described by Komninos et al. [12]. For each solution corresponding to the "2s2", "2p2" and "2s2s" states, we obtained all the other correlated roots. Then, these were allowed to mix via the continuum to first order in the reaction matrix (Eq. (14) of Ref. 12).

The results of our two types of computation are presented in Table 2 together with the experimental values. The discrepancy for the lowest $^1S$ state should be noted.

### Table 2. Widths from this work (in eV) and comparison with experimental values

<table>
<thead>
<tr>
<th>Isolated resonance (Eq. 4)</th>
<th>Inclusion of higher order effects (see text)</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s2 1S</td>
<td>0.114</td>
<td>0.138±0.015 (Ref. 60)</td>
</tr>
<tr>
<td>2p2 1S</td>
<td>0.012</td>
<td>0.138±0.015 (Ref. 61)</td>
</tr>
<tr>
<td>2s2s 1S</td>
<td>0.022</td>
<td>0.041±0.004 (Ref. 60)</td>
</tr>
<tr>
<td>2s2p 1P0</td>
<td>0.0093</td>
<td>0.015 (Ref. 60)</td>
</tr>
<tr>
<td>2s2p 1P0</td>
<td>0.038</td>
<td>0.038±0.004 (Ref. 59)</td>
</tr>
</tbody>
</table>

### Table 3. Widths of He doubly excited states by a variety of many-electron approaches (in eV)

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>(f)</th>
<th>(g)</th>
<th>(h)</th>
<th>(i)</th>
<th>(j)</th>
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</thead>
<tbody>
<tr>
<td>2s2 1S</td>
<td>0.125</td>
<td>0.124</td>
<td>0.343</td>
<td>0.123</td>
<td>0.094</td>
<td>0.117</td>
<td>0.117</td>
<td>0.107</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2p2 1S</td>
<td>0.0067</td>
<td>0.0073</td>
<td>0.0062</td>
<td>0.0059</td>
<td>0.0078</td>
<td>0.011</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2s2s 1S</td>
<td>0.039</td>
<td>0.036</td>
<td>0.058</td>
<td>0.037</td>
<td>0.041</td>
<td>0.041</td>
<td>0.038</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2s2p 1P0</td>
<td>0.0036</td>
<td>0.0034</td>
<td>0.0037</td>
<td>0.041</td>
<td>0.0079</td>
<td>0.0099</td>
<td>0.0093</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Bhattacharyya and Temkin (Ref. 20) - Golden rule
(b) Rehmas and Berry (Ref. 4) - Golden rule
(c) Burke and Taylor (Ref. 17) - Scattering phase shift
(d) Connolly and Lipsky (Ref. 3) - Golden rule
(e) Ho (Ref. 21) - Complex coordinate rotation
(f) Ramaker and Schrader (Ref. 26) - Multichannel CI with HF basis sets.
(g) Nikolaides and Adamides (Ref. 62) - Complex coordinate rotation
(h) Hildeman, Isaacson and Miller (Ref. 63) - Complex coordinate rotation
(i) Drake and Dulgar (Ref. 64) - Golden rule
(j) This work - For the 1S states it includes coupling of resonances via the continuum.
In Table 3 we present a number of theoretical results from a variety of advanced methods. The reduced Rydberg energy for He was used 1 Ry(He) = 13.60398 eV.

III. Conditional Probability Densities

We now turn to the use of our correlated DES functions for the computation and analysis of the conditional probability density, defined as

$$\rho(r_2, \theta_{12}|r_1=a) = \frac{\rho(r_1=a, r_2, \theta_{12})}{\int dr_2 d\theta_{12} \rho(r_1, r_2, \theta_{12})}. \tag{18}$$

$$\theta_{12}$$ is the interelectronic angle, and $$a$$ is a fixed distance from the nucleus.

Plots of $$\rho$$ have been examined extensively [1–3]. Conclusions were drawn as regards the models proposed by Kellman and Herrick [7, 8] about the triatomic molecule-like spectra and the “collective” motion of DES. The object was to recognize from the spatial forms of $$\rho$$, motion connected with rotations and vibrations of a linear triatomic ABA molecule.

The wave-functions which were employed in Refs. 1–3 were obtained from configuration-interaction calculations with Hylleraas or Sturmian basis sets using the stabilization method [18, 49, 55].

In order to obtain additional information about $$\rho$$ for the DES studied in Refs. 1–3, we have calculated Eq. (18) at the following levels of approximation

a) Use of $$\Phi_{FS}$$ with hydrogenic orbitals. b) Use of $$\Phi_{FS}$$ with MCHF orbitals. c) Use of $$\Psi_0$$, i.e. the fully correlated square integrable function (without the Rydberg series).

The importance of case (a) lies in its simplicity and in the fact that hydrogenic functions have been used for classification and computation of DES [22, 23].

The importance of case (b) lies in the fact that, because of the nature of the MCHF theory, the concerted, self-consistent motion of the two electrons with the same term expansion as that of the static hydrogenic approximation is taken into account. The difference between (a) and (b) is a measure of dynamic effects.

Case (c) aims at providing an accurate $$\rho$$, calculated according to the approach outlined in Sect. II.

Fig. 1. Conditional probability density distribution $$\rho(r_2, \theta_{12}|r_1=a)$$ for the He 2s^2 1S state at selected values of $$a$$. (All distances in atomic units). a Approximate Fermi-Sea vector (2s^2 + 2p^2) with hydrogenic orbitals. b Fermi-Sea vector (2s^2 + 2p^2) with MCHF orbitals. c–h Fully correlated square-integrable function (Fermi-Sea MCHF + correlation up to g orbitals). The graphs shown here are identical to those of Ref. 9.
Our results are given in Figs. 1–4. For reasons of economy, all three cases are presented only for the lowest $^1S$ DES (Fig. 1). It can be seen that the two-term $\Phi_{FS}$ yields a shape similar to that of $\Psi_0$. When the MCHF approximation is used even the volumes of cases b and c are very close. This is not true for case a. Our results from $\Psi_0$ and those of Rehmus, Ezra and Berry [1–3] are essentially identical.

Figure 2 presents only the $\Psi_0$ result for "2p$^2$" and Figs. 3 and 4 give only case b for reasons of economy, since we expect no substantial changes from the $\Phi_{MCHF}$ to the $\Psi_0$ densities.

Finally, Fig. 5 presents the averaged probability densities

$$
\rho_{Av} = \int_{0}^{\infty} dr_1 \rho(r_1, r_2, \theta_{1z})
$$

(18a)

for the $2s^2$ and $2p^2\,^1S$ DES using the fully correlated functions $\Psi_0$. 

---

**Fig. 2.** Conditional probability density distribution $\rho(r_2, \theta_{1z}|r_1 = \infty)$ for the He $2p^2\,^1S$ state at selected values of $\alpha$. (All distances in atomic units). Fully correlated square-integrable function (Fermi-Sea MCHF + correlation up to $g$ orbitals). The graphs shown here are identical to those of Ref. 9.

**Fig. 3.** Conditional probability density distribution $\rho(r_2, \theta_{1z}|r_1 = \infty)$ for the He $2s\,2p\,^1P^0$ state at selected values of $\alpha$. Fermi-Sea MCHF wave-function ($2s\,2p - 2p\,3d$) (see text).
IV. Differential Transition Amplitudes. Differences with Previous Work

Rehmus and Berry [4] have computed for the $2s^2$ and $2p^2\, ^1S$ DES in He the quantity

$$D(r_1, r_2, \theta_{12}) = r_1^2 r_2^2 \Psi_0(r_1, r_2, \theta_{12}) H U_K(r_1, r_2, \theta_{12})$$  \hspace{1cm} (19)

called the differential transition amplitude and have offered pictures and interpretations of interelectronic interactions as regards the dynamics of autoionization. The width $\Gamma$ is given in terms of $D$ as:

$$\Gamma = 2\pi \left| \int_0^\infty dr_1 \int_0^\infty dr_2 \int_0^\pi d\theta_{12} \sin \theta_{12} D \right|^2.$$  \hspace{1cm} (20)

$D$ was analysed in terms of the relative spatial positions of the three interacting particles and in terms of the contributions from the one electron and the two electron operators. $\Psi_0$ was computed from a Hylleraas basis set while $U_K$ was assumed orthogonal to $\Psi_0$ and given as an antisymmetrized product of $\text{He}^+ 1s$ and a "phase-shifted Coulomb function with corrective terms to handle the behavior at small distances".

Their results and analysis led them to several conclusions among which the most striking (to us) was that the dominant contribution to $\Gamma$ comes from the one-electron operators via a "generalized $S_N-2$ mechanism". The results of our analysis strongly contradict this picture as well as other observations made by Rehmus and Berry [4, 5].

In our work, $D$ is computed from

$$D(r_1, r_2, \theta_{12}) = r_1^2 r_2^2 \Psi_0(r_1, r_2, \theta_{12})(H - E_0)$$  \hspace{1cm} (21)

i.e. the full transition operator $(H - E_0)$ is used since $\Psi_0$ and $U(E_0)$ are made up of different basis functions which are not orthonormal between them.

The very fact of the (small) difference in the two expressions for $D$ suggests from the beginning that the breakdown of the overall quantity $D$ (whose square is an observable) into contributions from parts of the coupling operator is basis set dependent – regardless of the size and the accuracy of the total calculation.

In our case, the overlap corrections resulting from nonorthonormality are an inevitable but also physically meaningful result of the state-specific nature of our theory which accounts for relaxation at the orbital as well as at the correlation level [12, 13, 27, 33, 41, 45].

Our calculations have employed the $\Psi_0$ functions discussed in Sects. II and III and a Hartree-Fock
scattering orbital obtained in the field of He\(^+\) 1s. As an additional check of our overall numerical procedures the widths of Table 2 were obtained again, by direct integration of \(D\).

Our results for \(D\) are of two types. The first includes the term \(\sin\theta_{12}\) arising from the Jacobian. This is done because we believe that a more appropriate quantitative understanding of the spatial dependence of the transition matrix element is obtained when \(\sin\theta_{12}\) is included. Thus, in Figs. 6–9 we plot

\[D' = \sin\theta_{12}D\]

for the four functions \(2s^2, 2p^2\ \lower{1.5pt}\textstyle{1S}, 2s\ 2p\ \lower{1.5pt}\textstyle{3\!\!1P^0}\).

On the other hand, since Rehmus and Berry have computed \(D\) for \(2s^2\) and \(2p^2\ \lower{1.5pt}\textstyle{1S}\), we have also produced \(D\) for these two states in order to facilitate direct comparison. Figure 10 shows a comparison for the \(2s^2\) DES for \(r_1 = 0.5\) a.u. and \(r_1 = 1.5\) a.u.

Finally, Fig. 11 shows the averaged \(D'\) for the two \(\lower{1.5pt}\textstyle{1S}\) DES defined by

\[D' = \int_0^\infty dr_1 D'.\]  

**Discussion and Comparison with Ref. 4**

We present the analysis of our results by simultaneously comparing with the conclusions of Rehmus and Berry [4] who have offered mechanistic interpretations of autoionization based on the various contributions to \(D\).

The first point to mention is the fact that the widths, i.e. the integrated \(D'\)'s, obtained by the two approaches are essentially the same (Table 3).

However, quantitative as well as conceptual differences exist in the analysis of \(D\).

The first major difference concerns the conclusion of Rehmus and Berry that the dominant contribution to autoionization can be interpreted mechanistically as a “generalized \(S_n - 2\) mechanism” (a name borrowed from organic chemistry), caused by the large contribution of the one-electron operators. This finding struck us from the beginning as very surprising. For example, if a very large CI wave-function with hydrogenic functions were used [22] for the initial state and a hydrogenic continuum were used for the \(1s\,\text{SE}\) state, the one electron and overlap operators would have zero contribution to \(\Gamma\) and autoionization would seem to occur ex-
clusively via the two-electron repulsion operator. For the systems studied it did not seem that, by increasing the accuracy of the hydrogenic CI via final state mixing, deviations from such a picture could be so drastic as to nearly eliminate (only 10–15\% contribution was found in \cite{4,5}) the interelectronic repulsion contribution. As Rehmus and Berry \cite{4} state (p. 421–422), the \(1/r_{12}\) coupling implies a mechanism of two body collisions, while the \("S_{N}-2\) mechanism requires interaction of all three particles and hence is a three-body mechanism". Yet, one would expect from classical statistics two body collisions to provide an overall larger: probability for such simple systems. Of course, such classical reasoning is simplistic. Nevertheless, our results show that the main source of the autoionization rate is the \textit{interelectronic repulsion} (coupled with notions of overlap discussed below).

The second difference has to do with the relative importance of parts of the configuration space as regards their contribution to the differential amplitude of autoionization via the one- or two-electron operators. One electron operators effects are small after integration but not so necessarily in the differ-
below – is in the large values of the two-electron terms. This is in direct contrast to the findings and conclusions of Rehms and Berry who observed a large angularly isotropic contribution near the nucleus and explained it (Ref. 4, p. 419) by attributing to the Hamiltonian isotropic characteristics via the (unjustifiable) neglect of $1/r_{12}$. This large isotropic contribution was caused by the one-electron terms and hence their proposal for the three-body mechanism of autoionization.

The explanation of our findings is as follows: $U(E_0)$, i.e. the product of the He$^+$ 1s orbital with the scattering orbital, is large at small values of $r$, near the maximum of the core orbital. Similarly, $\Psi_0$ has considerable density at small $r$ slightly skewed toward $\theta_{12}=0$. Therefore, in the case of $2s^2 \, 1S$ state, there is significant probability of simultaneous penetration of the two electrons close to the nucleus. (In other words, the initial and the final states resemble each other when both electrons are close to the nucleus). This proximity of the two electrons makes the overlap $\Psi_0(1/r_{12}) \, U(E_0)$ large in this region and peaked toward the $\theta_{12}=0$ part. This contribution to the width could be interpreted mechanistically as the effect of very efficient electron-electron collisions which occur near the nucleus, where the Coulomb repulsion is sufficient to expel one electron which is in a bound orbital into a similar asymptotic one.

This picture is in accordance with the statement by Cooper, Fano and Prats [56] “an electron can be propelled by Coulomb repulsion to the high speed of the free state only in a region sufficiently close to the other electron”.

Finally, as regards the one-electron operators, it appears that the kinetic energy term, which is important near the nucleus, interferes destructively with the also important nuclear attraction term, with a result of an overall small contribution to $D$.

The second important region is around intermediate $r_1, r_2$ ($1–2.5$ a.u.) and much wider $\theta_{12}$. Mathematically, it arises from the small but non-zero net sum of the kinetic and potential energy terms, operating on the two-electron continuum function, multiplied (and enlarged) by a very high rotor-like $\Psi_0$. A significant peak at $r_1=r_2$ also appears as the combination of a rather loose repulsive effect, weighted by the large value of $\Psi_0$, and cancelled partially by the negative (there) one-electron terms. Such contributions do not appear at all in Ref. 4. In fact, these authors reported a damping of the integrand when either electron is at $r > 1.5$ bohr, which they ascribed to the “$1/r$ dependence of the scattering function”. However, one may argue that the differential transition amplitude contains, by definition, an $r_1^2 r_2^2$ factor, and, since the final state scatter-
Fig. 10a and b. Comparison of the differential transition amplitude, $D$, as given by Ref. 23 to that obtained in this work, Eq. (21), for the He $2s^2$ $1S$ state at $r_1 = 0.5$ and 1.5 a.u. b This work, Ref. 23. The differences are stated in Table 4.

ing function reduces to a single product at large $r$, the whole integrand is expected to vanish only due to the damping of $\Psi_0$, which however, occurs at much larger distances ($r > 4$ bohr).

In conclusion, our analysis of $D$ for $2s^2$ suggests a cause for large autoionization which is probably universal: Simultaneous penetration of two electrons in a small region of space close to nucleus where the core orbital of the ion times the scattering orbital have significant overlap with $\Psi_0$ at $\theta_{12} \to 0$. DES lacking this property will exhibit smaller widths. We emphasize that we refer to the "close to nucleus" region because for the He DES, the core orbital of the ion accumulates its amplitude in this region. In other cases (consider for example the Ne $1s^2 2s^2 2p^2 3s^2 1S$ DES) the core orbitals may concentrate further out and thus the region of space important for autoionization may involve larger $r$.

The validity of this proposal is borne out by our calculations on the other low lying DES of He+ as can be readily verified by inspection of Figs. 7-9. For example, the $2p^2$ $1S$ state is known to have a much smaller (about one order of magnitude) width compared to the otherwise similar $2s^2$ state. According to our analysis, this difference is ascribed mainly to the negligible density of $\Psi_0$ for $2p^2$ at small $r$ and $\theta_{12} \to 0$. It is also due to the fact that whereas for the $2s^2$ state the differential terms add constructively, ($D$ is positive everywhere), for the $2p^2$ state destructive addition of the differential terms reduces the width further. On the other hand, the $2s^2 2p^1p^0$ DES, for which the probability density plots suggest inter-
mediate penetration, (smaller than in the $2s^2$ state but larger than in the $2p^2 \, ^1S$ state), exhibits a width that lies between the $2s^2$ and $2p^2 \, ^1S$ values.

Finally, as a corollary to our proposal appears to be the fact that triplet states have a smaller probability of autoionization. This is a result of the exclusion principle which introduces a Fermi hole in the wave-function, thus not allowing the two electrons to come close to each other.

On the basis of different relative penetration of $\Psi_0$ to the small $r$ region and its effect on the magnitude of the autoionization width, we may in general anticipate that He DES composed of higher $l$ orbitals will exhibit narrower widths. For example

$$\Gamma(mpnp, \, ^1S) < \Gamma(msnp, \, ^1P^0)$$

$$< \Gamma(msns, \, ^1S), \quad n \geq m \geq 2.$$  

As regards relative widths for Rydberg series, such as those examined by Rehmus and Berry [4], our predictions for singlet states are

$$\Gamma(2msns, \, ^1S) < \Gamma(2s^2, \, ^1S), \quad m > n > 2$$

$$\Gamma(2pmpn, \, ^1S) < \Gamma(2pnp, \, ^1S)$$

$$< \Gamma(2p^2, \, ^1S), \quad m > n > 2.$$  

The above mentioned observations concerning the $l$ as well as the symmetry dependence of the width are in agreement with those reported by Mozeyev and Weinhold [57].

A final point, on the suggestions [1, 5] relating the probability of autoionization to the so-called rotor-anitrotor classification [7, 8] is worth making. The herein proposed mechanism is based on the existence or not of considerable charge density at small $r_1, r_2, \theta_{12}$. On the other hand, such classifications are made by studying the wave-functions at larger distances, usually near the most probable $r$. Thus, it appears to us that the molecular classifi-

cation schemes and the dynamics of autoionization need not coincide in general.

The results and main conclusions from our analysis and from that of Rehmus and Berry [4, 5] are collected in Table 4.

VI. Synopsis

We have tested and demonstrated the utility of a state-specific approach to the wave-mechanics of low-lying doubly excited states of He, where the zeroth-order wave-function is obtained at the MCHF level and where the correlation functions are optimized variationally. Both zeroth-order and correlation functions are made orthogonal to core orbitals corresponding to open channels. The simple Fermi-Sea MCHF functions are easy to interpret according to the "rotor-antirotor" classification of these DES [2, 3, 7, 8]. The localized correlated functions, $\Psi_0$, are small but accurate. It is found that within the frozen-core HF approximation, high lying Rydberg configurations leading to an open channel should not be included in $\Psi_0$ when calculating the width according to (4).

Our numerical results consist of energies, widths and probability amplitude and density plots. The width calculations for the $^1S$ states, $2s^2$, $2p^2$, and $2s \cdot 3s$, have taken into account resonance-resonance interactions via the continuous spectrum. As regards the observables, energy and width, the agreement of our results with previous theoretical and experimental values is very good except for the width of the lowest $^1S$ DES where some discrepancy exists. However, as regards our interpretation of the dynamics of autoionization, it differs from the one presented a few years ago by Rhemus and Berry [4]. Our results suggest that nonrelativistic autoionization is mediated primarily via the two-electron operator and involves the simultaneous penetration of the two electrons in a region where the core orbital of the ion times the scattering orbital have significant overlap with $\Psi_0$ at $\theta_{12} \rightarrow 0$ (see Table 4).

Finally, we point out that the generality of the present approach to the effective solution of the Schrödinger equation for excited states has allowed the development of convenient formulations for a) the prediction of the relativistic structure and lifetimes of autoionizing states in neutral atoms and negative ions [24, 25, 58] and b) the development of a theory of a special class of high-lying DES which constitute the two-electron ionization ladder (TEIL) leading, as a function of the principal quantum number $n$, to the threshold for two-electron ionization [32].
Table 4. Results on the $^3S$ He DES and proposals for the mechanism of autoionization

<table>
<thead>
<tr>
<th>Similarities</th>
<th>Rehmus and Berry (Ref. 4)</th>
<th>This work</th>
</tr>
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<tbody>
<tr>
<td>Square-integrable functions</td>
<td>see plots of Figs. 1 and 2</td>
<td>see Table 2</td>
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<td>Calculated widths</td>
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</thead>
<tbody>
<tr>
<td>Major contribution to width</td>
</tr>
<tr>
<td>One-electron operators</td>
</tr>
<tr>
<td>Two-electron operator</td>
</tr>
<tr>
<td>Short-r region of space</td>
</tr>
<tr>
<td>Large angularly isotropic amplitude (</td>
</tr>
<tr>
<td>Large amplitude skewed toward ( \theta_{12} = \theta ) (Very important collisional effect weighted by an appreciable spherically symmetrical charge density)</td>
</tr>
<tr>
<td>Medium-r region of space</td>
</tr>
<tr>
<td>Vanishing amplitude (attributed to the &quot;for dependence of the scattering function&quot;)</td>
</tr>
<tr>
<td>Large amplitude skewed toward ( \theta_{12} = \pi ) (Attributed to kinetic energy operator terms weighted by a high probability density)</td>
</tr>
</tbody>
</table>

References

29. Solutions based on analytic functions require a good deal of computational experimentation. Although less accurate, they have the occasional advantage of permitting convergence to local minima but no guarantee of correctness possible. (The virial theorem, number of nodes (when applicable) and orbital occupancy must be taken into account. On the other hand, numerical solution of the 11F, MCHF equations for negative ion or highly excited DES, when possible, are reliable but require tedious and sensitive integration procedures
54. The case of all channels open with prediagonalized function spaces was first given formally by Fano, U., Prats, F.: Proc. Natl. Acad. Sci. (India) A33, 553 (1963); Later, Ramaker and Schrader (Ref. 26) dealt with the problem of prediagonaliz-
tion and applied a multichannel configuration-interaction theory to the He$^1S$ states with HF bound functions and screened hydrogenic scattering orbitals.


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