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Theoretical Approach to the Calculation of Energies and Widths of Resonant (Autoionizing) States in Many-Electron Atoms

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A theoretical approach, capable of providing quantitative results for N-electron nonrelativistic "nonstationary" states is presented. I treat inner-hole or doubly excited states, observed in various types of experiments, from a conceptually single point of view, as decaying states. First, the relevant important quantities already known, e.g., from Feshbach's theory, are derived and interpreted in a mathematically and physically meaningful way. Then I consider the exact square-integrable N-electron function describing the initial localized N-electron state and, from straightforward variation-perturbation-theory considerations, I derive a variational minimum principle which permits one to incorporate systematically the important correlation effects without the danger of a "variational collapse." This method requires projection onto known one-electron zeroth-order functions and it thus overcomes the difficulties of the well-known P, Q methods which require projection onto exact wave functions. From preliminary N-body calculations I find the He$^-$ $^2P^0$ and ^2D resonances, previously observed experimentally, at about 57.3 and 58.4 eV. In addition, I predict the positions of various autoionizing states: in Li I at about 140.7 eV (a $^2P^0$ state), in C IV at about 306.7 eV (^2D), in N I at about 14.9 eV (^2D), and in F I at about 22.4 eV (^2S) above the ground state. These states, which are just samples of states treatable by this approach, may in principle cause observable structures, e.g., in photon-absorption experiments, in particle-atom scattering experiments, or in beamfoil experiments.

I. INTRODUCTION

When considering an isolated N-electron atomic system, with the idealization that there is no interaction with the radiation field, experimental evidence suggests that its excited states may physically be divided into "stationary" and "nonstationary" states. The above idealization dropped, the "stationary" states can be observed, e.g., through the well-known methods of optical spectroscopy, and have formed the basis for the development of the foundations as well as of the calculational methods of quantum mechanics. The "nonstationary" states are different in that they are observed through electron emission. Physically however, the reasons for the "mechanism" of these processes appear to be similar. Consider, for example, the time developemnt of the process after excitation has occurred. The excited state of the dynamical system at an instant of time $t=0$ may interact not only with the continuum of the electromagnetic field but also, if symmetry and energy considerations permit it, with the continuum of an "electron field." The result of such an interaction is a transition between two states with photon emission (radiative transitions) or electron emission (radiationless transitions), or both, and a very small "level shift" in the energy of the initial state. In mathematical language this interaction can be considered as a small perturbation on the Hamiltonian of the initial state of the system. In fact, to paraphrase Dirac,[1] the meaning of such phenomena can be given only with reference to a perturbation method. The perturbation for radiative transitions may be taken as external to the dynamical system and written down explicitly. The perturbation for radiationless transitions however is due to the electron Coulomb interaction itself and can be thought of as being caused by a very small instanteous "residual" electron-electron repulsion force, whose explicit form is unknown.

From another point of view,[2] that of scattering, some of the "nonstationary" states of an N-electron atom are in principle observable in collisions of particles with a target atom. In such cases, the incoming wave packet is thought of as being momentarily caught in a potential of finite barriers, and a time delay in its emergence occurs. Experimentally, this can be observed, e.g., as a peak in the reaction cross section at a certain energy since the ratio of the intensities of the outgoing and incoming waves becomes singular when there is only an outgoing wave. As is well known, mathematically this corresponds to a pole of the S matrix in the lower-half of the complex energy plane, with the phase shift rapidly increasing with increasing energy through $\frac{1}{2}\pi$ (modulo π).[2]

Depending on the physical picture one adopts or on the experimental method of observation, the "nonstationary" states are usually called Auger, x-ray, autoionizing, compound or resonant states. Most often, the use of Auger and autoionizing implies a bound-state point of view, whereas compound or resonant imply a scattering point of view. In principle, they can be assigned an energy E, a decay width Γ, and quantum numbers of total angular momentum and spin. Furthermore, in most cases, they can also be assigned a "configuration" according to Bohr's concept of the central field. When such a configurational assignment is made, they may correspond to singly, doubly, or triply excited states of neutral atoms or of negative or positive ions.

Such states were first observed and interpreted more than 40 years ago through x-ray spectroscopy, absorption spectra, and scattering experiments.[3] In recent years, the variety and frequency of experimental observation of such states have increased immensely. To refer to only a few, there have been photon-absorption spectroscopy experiments[4] in the uv and far uv on inert gases, alkali-metal and alkaline earths as well as other species; particle-atom collision experiments[5]; beam-foil spectroscopy experiments[6]; x-ray-Auger-spectroscopy-type experiments.[7]

Within the central-field model the "nonstationary" states in atoms may roughly be divided into two categories: (a) inner-hole states such as those observed in Auger phenomena (e.g., Coster-Kronig transitions) and (b) multiply (usually doubly) excited states with one or two outer electrons excited into higher—than those of the ground state—principal quantum number orbits. These states are associated with the conspicuous structures in the photoabsorption cross sections in the uv as well as with resonances in cross sections of scattering experiments.

For states of the first category, almost all of the existing theories are rather descriptive, that is they simply "explain" the process in terms of simple one-electron pictures.[8] The details of electron-electron interaction and their effects on experimental observations are thus not treated accurately. The states of the second category have attracted much more attention. Since similar resonant states appear in nuclear reactions also, the first general theories accounting for the mathematical and physical properties of such states were given in the context of nuclear physics, e.g., by Kapur and Peierls,[9] Siegert,[10] or Wigner and Eisenbud.[11] In atomic physics and chemistry, the early attempts to treat the observed phenomena quantum mechanically were those of Wentzel,[12] Rice,[13] and Fano.[14] It is only recently however that rigorous theories have been developed, mainly by Feshbach[15] and Fano[16] (see also Fonda and Newton[17] and Shore[18]). They provide the basis for the understanding and analysis of the properties of resonant states and their effects on photon-atom or particle-atom collision cross sections. The dynamical origin of the resonances is emphasized and the important observables are given in terms of matrix elements of the total or effective Hamiltonians.

The qualitative predictions of the above theories, for example Fano's parametrization of photon-absorption profiles, are in excellent agreement with experiment. From the quantitative point of view, however, that is the prediction of values for the positions and widths of nonstationary states of both categories for an arbitrary N-electron system, it appears that things are not as complete. The main difficulty is, of course, that one is dealing with an N-body problem with all its conceptual and computational complexities. In a rigorous theory, whether of the bound or scattering state point of view, the details of electron-electron interaction have to be accounted for. Furthermore, "nonstationary" states have peculiarities that ordinary "stationary" bound states do not have. They are highly excited, having an infinity of lower-lying states of the same symmetry. In many cases, e.g., negative ions of category II, their charge distribution is quite diffuse and relatively long-range interactions may be more important than in, for example, ordinary ground states. In the language of many-body theory,[19] this may imply that three-(or higher-)electron correlations could become significant. In addition, the useful property of one-to-one correspondence between reality and configurational assignment may in some cases be lost as one moves up in energy and the density of states increases. Also, from the mathematical point of view, they do not have the useful property of square integrability, having radiation boundary conditions. Thus, they do not form a complete orthonormal set and variational or perturbation theories dealing with such states must essentially be non-Hermitian in character.

There are many theoretical approaches to the calculation of energies and widths of nonstationary states. Some are rigorous, some are not. Most are readily applicable to two- or three-electron systems only. I review them in Sec. II, briefly examining their merits and limitations. For detailed accounts of certain experimental and theoretical methods, properties and classification of resonant states, as well as applications, the reader is referred to Refs. 7 and 8 for inner-hole states (see also Fano[22]) and the excellent review articles by Smith,[20] Burke[21] (see also Fano and Cooper,[22a] Chen,[23] and Holøien[23a]) and the book edited by Temkin.[24]

The purpose of this paper is to provide a conceptually self-consistent approach and its methodology in applying a general procedure to the calculation of wave functions, energies, and widths of an arbitrary N-electron nonstationary state of either category. My approach, first formulated some time ago elsewhere,[25] is based on a bound-state point of view. I consider the nonstationary states as decaying states having been formed by some excitation process whose effect on the energy and decay width (if any) is ignored. Only the localized component of the decaying state wave function is considered and calculated variationally, the component which, from the physics of the time-development of the system, at $t=0$ describes the dynamical state of the system completely. Using variation-perturbation theory, a general upper-bound variational principle, applicable to an arbitrary N-electron system, is then derived. Thus, based on this principle, variational calculations to obtain N-electron wave functions of highly excited states having an infinity of lower states of the same symmetry now become feasible. In this case, to systematically account for correlation effects, the non-closed-shell many-electron theory of Sinanoğlu and co-workers[26] is applied.

A few preliminary results on energy positions of certain autoionizing states in He$^-$($^2P^0$, ^2D), Li($^2P^0$), C IV(^2D), N(^2D) and F(^2S) are reported in this paper. For the He$^-$ states there have been experimental observations.[5] For the others there are none and hence our values herein constitute theoretical predictions of structure in reaction cross sections.

II. PREVIOUS THEORETICAL METHODS

One may divide the theoretical methods which have been applied to the nonstationary states into three categories: The first contains theories which treat the problem from the scattering point of view where the relevant quantities are usually found from their relationship to the energy-dependent phase shift. The second contains theories which attempt to solve directly for the decaying state energy and width from a complex eigenvalue equation. The third includes methods which, either explicitly or implicitly, treat these states as more or less ordinary bound states. The energy is obtained as the expectation value of the Hamiltonian with respect to a certain wave function and the width is given by a transition probability expression where the final state is described by a continuum wave function.

The most generally applicable and extensively used method of the first category for an arbitrary N-electron system is the close-coupling approximation and its modifications as applied mainly by Burke, Smith, and co-workers.[20,21,27] It essentially "repeats" the scattering experiment calculating the phase shift as a function of E. When the phase shift rises rapidly by π a resonance is located. The width is found by the use of equations relating it to the phase shift. The method is versatile and yields a large amount of information off and on resonance. It is rigorous yet it suffers from calculational inadequacies. Even for a few electron systems the computations become enormous. Electron correlation has to be properly taken into account. The calculations by Burke and Taylor[28] were a first step toward that direction. However, there are still no *a priori* conditions on how to perform an accurate calculation including the details of electron-electron interaction. For example, results on nitrogen show that widths may vary by an order of magnitude as a function of the number of terms included in the close-coupling expansion.[29]

Resonances can also be found as poles of the S-matrix using Faddeev's equations as in the work of Ball, Chen, and Wong.[30] These methods, however, are limited to two-electron systems. Finally, the M-matrix formalism,[31] an adaptation of the Kohn variational principle by Nesbet and its extension to the calculation of resonances[32] and the algebraic methods of Harris and Michels,[33] are all in principle capable of treating the resonances accurately if suitably chosen wave functions are used. Here, however, one should note that Shimamura[34] has recently pointed out that the last two theories and similar expansion methods may sometimes have the disadvantage of predicting "nonphysical" pseudoresonances. This problem has also been treated by Harris and Michels.[35] Thus far, results have been reported for resonances in two-electron systems only.

Dealing directly with the decaying states, Herzenberg, Mandl, Bardsley, and Kwok[36] have developed a general theoretical approach based on an adaptation of the Kapur–Peierls theory. Through an iterative variational procedure, a stationary (but not with an upper-bound property) value for a complex energy is obtained which yields both the energy and the width of the resonance. The method has been applied to e^--H and e^--He scattering. Its accuracy, however, has as a prerequisite the existence of good wave functions, which is a problem by itself. For $N>3$, where simply parametrized, good analytical wave functions are not easily obtainable, this method may not be readily applicable. When applied in an approximate manner, it also has the disadvantage of being R dependent and Taylor[37] has argued that with accurate wave functions the results are sensitive to the adopted radius of region of interaction. Nevertheless in the limit the method is in principle R independent and when properly used it can provide much information about Feshbach or shape resonances in atoms or molecules with a few electrons.

Finally, there are the methods of category III. As a first approximation to E and Γ, orbital approximation wave functions, containing simple analytical, screened hydrogenic or other one-electron functions created from various local or nonlocal potentials, may be employed. Such is the case for several "inner-hole-states" theoretical approaches[8] used to calculate the important observable quantities. Even approximate configuration-interaction studies[38] have indicated the inherent limitations of the above methods. There is obviously a need for the application of theories which would account, whenever necessary, for electron correlation and continuum effects systematically. For high Z, the important relativistic effects require the development of a relativistic electron correlation theory.[39] Orbital approximations have also been used for doubly excited states since the 1930's especially in the pioneer work of Wu and collaborators.[40] The energy was simply the expectation value of the Hamiltonian and the width was calculated by the Golden-Rule-type formula Wentzel[12] first gave for radiationless transitions, where the total Hamiltonian is written as $H = H_0 + 1/r_{12}$, and $1/r_{12}$ is treated as a perturbation (not small!) to first order. Their approach was later criticized by Bransden and Dalgarno[41] who proposed a variational method for the computation of the widths. Similar independent-particle model calculations have been reported on helium and larger systems by Wu and Ourom,[42] Propin,[43] Manson,[44] Ramaker, Stevenson, and Schrader[45] and others. Such methods do not account for electron correlation in the discrete or in the continuum spectrum. Furthermore, when the one-electron functions are parametrized and obtained variationally no proof for the important minimum property of the calculated energies is provided.[43] Yet, one can show, as in the case of an arbitrary excited bound state,[25,46] that such a property for independent-particle model functions is satisfied as long as the configurational assignment is correct and the orbitals have the proper $O(3) \times SU_2$ symmetry and radial nodes.

To obtain reliable quantitative results, in principle one has to improve upon the independent-particle approximation. This can be done by perturbation or variation methods or their equivalent. Variations of the perturbation theory have been applied, for example, by Sharma and Wilson[47] and Drake and Dalgarno[48] but only for two-electron systems. The most extensive perturbation calculations yet have been carried out by Safronova, Kharitonova, Matulis, and co-workers.[49] They have provided a large number of reasonably accurate energies (and certain widths) for various N-electron states of low-Z atoms and ions with inner holes or doubly excited electrons, in principle observable in different kinds of experiments. Similar, but not as extensive, calculations were also performed by Chase, Kelly, and Köhler using Kelly's adaptation of the Brueckner–Goldstone theory.[50] Convergence problems and insufficient consideration of the adjacent continuum may be the only drawbacks of these methods. Other many-body approaches have been developed mainly by Brandt and Lundqvist,[51] Amusia and co-workers,[52] and Wendin[53] and may prove very useful, qualitatively and quantitatively especially for high-Z atoms where collective excitations may be important.

The alternative to the perturbation theories are the numerous and better-known variational or configuration-interaction techniques. These methods can be considered as applications of the general theories of Feshbach[15] and Fano.[16] According to Feshbach's theory, the unique definition (but not unique existence) of a projection operator P projecting asymptotically onto the open channels has helped present the resonance problem clearly. Some of the main quantities in this theory are (a) the eigenfunctions and eigenvalues of the "QHQ Hamiltonian," the definition of which is not unique due to the arbitrary choice of the Q projection operator, (b) the "level shift" Δ, which is given as a principal-value integral and corrects for the inaccuracy of the eigenvalues of QHQ due to the interaction with the continuum, and (c) the width Γ given from a Golden-Rule-type formula. The first rigorous application of this theory to atoms is due to O'Malley and Geltman[54] who adopted a special definition of P from Hahn, O'Malley, and Spruch[55] and applied a rigorous variational principle for two-electron systems. Instead of requiring P to project asymptotically onto the open channels, they took P to project onto the ground state for all values of r. Although such an assumption is not required in the Feshbach formalism, it produces the correct conditions for a treatment of the problem by the ordinary upper-bound variational method in the Hilbert space of square-integrable functions. One note that the autoionizing states have an infinity of lower states of the same symmetry, a fact which renders ordinary variational minimum principles inapplicable. For two-electron systems, the ground state of the "target" is known exactly and the method is rigorous. Its accuracy depends on the accuracy of the wave function involved. The energy E_Q of the QHQ Hamiltonian is evaluated and is related to the resonance energy E by $E = E_Q + \Delta$. Δ however is not uniquely defined. Its magnitude depends on the details of the Q operator while its sign may be positive or negative so that formally, no upper bound to E can in principle be obtained. Nevertheless, for light atoms Δ is small (see Ref. 56 and the Appendix) and an accurate E_Q can for all practical purposes represent E. Accurate calculations based on the elegant P, Q formalism have been carried out also by Bhatia and Temkin,[56] Chan and Stewart,[57] Chen and

Rotenberg,[58] and others. However, for systems with more than two electrons the method is not applicable. This is because, as well known,[54,55] the formalism requires the knowledge of *exact* target wave functions, which is feasible only for hydrogenic targets. And unless there are restrictions imposed on a variational or configuration-interaction (C.I.)-type calculations, one cannot be certain of the final answer since, in principle, such calculations would tend to lower the total energy to the energy of the ion in its ground (excited) state and a free electron of zero kinetic energy.[43,59] An alternative approach, with the much desired upper-bound property, has been formulated by Perkins[60] and applied to C.I. calculations by Holøien and Midtdal.[61] However, this method also is rigorous only for two-electron systems.[60,61]

The Fano method of C.I. of zeroth-order discrete and continuum states has also been applied by Altick and Moore[62] and Altick[63] who used hydrogenic and Hartree–Fock functions to compute energies and transition probabilities in helium and beryllium. Their approach, as a direct application of the Fano theory, is rigorous and in principle can provide all the important information pertinent to autoionizing states exactly. No results have been reported for larger systems where accurate computations appear to be a formidable problem. An approximation to the Fano method is the so-called "truncated diagonalization" or "stabilization" method, applied to two- and three-electron systems by Lipsky and Russek,[64] Holøien and Midtdal,[65] Miller,[66] Taylor and collaborators,[37,67] Eliezer and Pan,[68] and others. The method is similar to the QHQ method only that no specific form of Q is assumed. One just diagonalizes a big, "properly" chosen basis set of square integrable functions and by adding or subtracting terms, sees how certain roots of the secular equation "stabilize" that is, are not affected by the addition or removal of basis functions. One then makes the correspondence of stabilized roots with resonance energies. Here one may note that a "stabilization" method cannot rigorously guarantee upper bounds and it may often stabilize a root which does not even correspond to a true resonance.[34,68] Furthermore, its experimental-type approach renders its application to an arbitrary N-electron system rather difficult. A good mathematical analysis of the "diagonalization" methods and their implicit simplifications of the Fano theory with regards to the coupling between closed and open channels has been given by Balashov *et al.*[69] These authors found that, for two-electron systems "neither the coupling of the closed channels through the continuous spectrum nor the modification of the functions of the resonance levels by the open channels play a substantial role."

I have referred to most of the theoretical methods applied to the study of autoionizing states. I conclude that, beyond the not too accurate independent-particle model, most of these, either because of the general difficulty of the N-body problem or because of their inherent limitations, have up to now been applicable only to two- or three-electron systems. In Sec. III I propose yet another theoretical approach, applicable to an arbitrary N-electron autoionizing state, which forms a basis for N-electron system variational calculations to complement scattering and perturbation methods.

III. PRESENT APPROACH

Before I present my arguments for the calculation of the important observables, I wish to consider a few real situations in the continuum of the spectrum of the total Hamiltonian: (a) There are atomic states which, although they energetically lie above the ionization limit, due to symmetry restrictions they are considered discrete, corresponding to square-integrable wave functions of the total nonrelativistic Hamiltonian H. Such states are, for example, the $1s^2 2s 2p^5\,{}^3P^0$ state of oxygen or the $1s2s2p\,{}^4P^0$ state of lithium. They decay through a radiative transition. When relativistic effects are taken into account, L-S coupling breaks down and spin-dependent forces may couple the initially "square-integrable" wave function to the adjacent continuum. A radiationless transition of low probability is then possible. Actually, such processes have recently been studied experimentally for $nsn'sn'p\,{}^4P^0$ states in the alkali as well as in He^- by Novick and collaborators.[70] (b) Consider an "Auger" state. Its lifetime is very short and, as well known, for small Z the dominating decay process is electron emission whereas for high Z, x-ray emission is observed. In many cases the phenomena are competitive. Thus, it appears that such decay processes may be taken to initiate from the same physical state. Its existence is experimentally verified by different types of observations depending on the rate of decay of each mode involved. Furthermore, since in the case of radiative transitions this state is described by a square-integrable wave function, it is reasonable to assume that for radiationless transitions also, the physical initial state is described by such a square-integrable wave function. (c) Finally, I mention the phenomenon of dielectronic recombination,[71] i.e., the inverse of autoionization, where a free electron and an ion combine to form a "nonstationary" state in the continuum which however now decays radiatively, like an ordinary discrete state.

The above samples of physical processes were given to point out that autoionizing states resemble ordinary bound states very much. In fact, the concept of "stationary" and "nonstationary" atomic states may often become rather loose since it depends on the physical Hamiltonian assumed or on the method of observation.[72] It is then apparent that, if one neglects the effects of the excitation mechanism on the observables E and Γ (experimental evidence supports this assumption), "nonstationary" states can be legitimately treated simply as decaying states in a time-dependent process caused by a weak perturbation and need not be approached only from a scattering point of view (where time goes from $-\infty$ to $+\infty$). That is, just as in ordinary (optical) excited states, one may consider specific initial and final states, assume their wave functions and energies as solutions of eigenvalue equations under special boundary conditions at infinity, and obtain the experimentally observed quantities by utilizing theory properly. Here, I should make it clear that the above considerations apply only to the so-called "Feshbach" resonances[20,21] which constitute by far the great majority of cases in atoms, and not to broad "shape" resonances whose existence is in principle verifiable only in scattering experiments.[73] With the above in mind, I turn to the mathematical formalism necessary for the identification and calculation of the relevant quantities.

A. Linewidth and Level Shift

Let the wave function describing the resonant state be denoted by $\psi(\vec{r})$. It satisfies the time-independent eigenvalue equation:

$$H|\psi\rangle = E|\psi\rangle \tag{1}$$

with the boundary conditions[10]

$$\begin{aligned} \psi(\vec{r}) &\to 0 \quad \text{as } r_i \to 0, \\ \psi(\vec{r}) &\sim e^{ikr_i} \quad \text{as } r_i \to \infty, \end{aligned} \tag{2}$$

where k is complex with $\mathrm{Re}\,k > 0$. The solution E of Eq. (1) is thought of as a complex eigenvalue in the second Riemann sheet with a small imaginary part corresponding to the resonance linewidth.

For any square-integrable wave function $\psi_0(\vec{r})$, the quantity $\langle\psi_0/\psi\rangle$ is finite and defined. Choose $\psi_0(\vec{r})$ to be the complete description of the state of the system at $t=0$. That is, I assume that, in a time-dependent picture $|\psi_0(r)\rangle$ describes the system at the instant of time ($t=0$) when it is prepared, and at that instant the state is localized. The wave function $\psi_0(\vec{r})$ must satisfy an eigenvalue equation:

$$H_0|\psi_0\rangle = E_0|\psi_0\rangle \tag{3}$$

with

$$\psi_0(\vec{r}) \to 0, \quad r_i \to 0, \quad \text{or } r_i \to \infty . \tag{4}$$

In S-matrix theory language, $|\psi_0\rangle$ is the time-delaying state which is coupled to the continuum to yield the time-delayed components of the reaction amplitude.

Form

$$Q = |\psi_0\rangle\langle\psi_0| , \quad P = 1 - Q . \tag{5}$$

It then follows that

$$H|\psi\rangle = (H_0' + V)|\psi\rangle , \tag{6}$$

$$\begin{aligned} H_0' &= QHQ + PHP = H_0 + PHP , \\ V &= QHP + PHQ , \end{aligned} \tag{7}$$

$$H_0'|\psi_0\rangle = H_0|\psi_0\rangle = E_0|\psi_0\rangle . \tag{8}$$

H_0' also has eigenstates in the function space orthogonal to $|\psi_0\rangle$. They are found in the continuum and are functions of the continuous parameter E which is related to the wave number k of the free particle by $E = (\hbar^2/2m)k^2$. To distinguish the different vectors belonging to the degenerate states at E, let α denote the totality of variables characterizing each eigenvector $U(E,\ \alpha)$. For an arbitrary functional space we have

$$H_0'|U(E,\ \alpha)\rangle = PHP|U(E,\ \alpha)\rangle = E_\alpha|U(E,\ \alpha)\rangle , \tag{9}$$

with

$$\langle U(E,\ \alpha)|U(E',\ \alpha')\rangle = \delta(E-E')\,\delta(\alpha-\alpha')\,h(U), \qquad h(U) > 0. \tag{10}$$

If $\rho_U(E)$ is the density of states then

$$\rho_U(E) = [h(U)]^{-1}\frac{dU}{dE} \tag{11}$$

and the projection operator P, for an energy region between E and $E+dE$ can be written as

$$P_{E_\alpha} = |U(E,\alpha)\rangle\rho_U(E)dE\,\langle U(E,\alpha)| . \tag{12}$$

In configuration space, the asymptotic normalization for the radial function of the free electron may be taken to be

$$R_{kl}(r) \sim \frac{1}{\hbar}\left(\frac{2m}{\pi k}\right)^{1/2}\frac{\sin(kr - \frac{1}{2}l\pi + \delta_l)}{r} \qquad \text{as } r \to \infty \tag{13}$$

with

$$\begin{aligned} \int_0^\infty dr\,r^2 R_{kl}(r) R_{kl'}(r) &= (m/\hbar^2 k)\delta_{ll'}\,\delta(k'-k) \\ &= \delta_{ll'}\,\delta(E'-E) . \end{aligned} \tag{14}$$

As usual, δ_l is the phase shift of the lth partial wave corresponding to the scattering of the free particle.

The wave functions $\psi_0(\vec{r})$, $\psi(\vec{r})$, and $U_{E,\alpha}(\vec{r})$, solutions of the time-independent eigenvalue equations (3), (1) and (9) under different boundary conditions, may now be used in describing the time evolution of the system. Here I emphasize that the state $|\psi_0\rangle$ is not an eigenstate of some unphysical (say interactionless) zeroth-order Hamiltonian. Rather, one has to think of it as time dependent which, at $t=0$, is localized and contains all the information about the interactions in the system. This assumption is supported by the experimental observations mentioned before. Furthermore, it is consistent with theories of the quantum mechanics of decaying states,[74] where the initially prepared state is always described by a square-integrable wave function. Under the influence of the perturbation V, defined by Eq. (7), a rapid irreversible process occurs where the system undergoes a transition into a state with a free particle at infinity. Furthermore, due to the coupling with the continuum, the initial energy E_0 suffers a shift Δ which in principle ought to be time (energy) dependent. One may then imagine that for $t\sim(0,\,\delta t)$ the energy changes by small increments $\epsilon(t)$ until an extremum is reached at which

$$\left.\frac{\partial E(t)}{\partial t}\right|_{t\geq t'}=0\ \ [\epsilon(t')=0],$$

and the state of the system is in the resonant state $|\psi\rangle$ with energy E. The wave function now is energy dependent in the complex energy plane (to satisfy the physics of the uncertainty principle), and has a small continuum component, a fact which, in the time-independent eigenvalue equation (1), is expressed by the outgoing-wave boundary conditions of Eq. (2). This nonstationary process may also be thought of, in a time-independent sense, as a superposition of stationary processes with different energies E. My choice to look at the physics as a time-dependent irreversible process is rather arbitrary.

The best way to express the above mathematically is to apply the quantum theory of damping as developed for matter-radiation interactions.[75,76] The concepts of transition and level shift are of course well accepted there and theoretical predictions agree with experiment to a high degree of accuracy. The approach is based on treating directly the integrated motion over a long (relatively) period of time with the final state having a particle at infinity.

According to my assumptions $|\psi\rangle$ of Eq. (3) $\equiv|\psi,\ t=0\rangle$. I am interested in the time development of the system under the time-independent perturbation $V=H-H_0'=QHP+PHQ$. Let $\psi(\vec{r},t)$ be the solution of the time-dependent Schrödinger equation for $t>0$ given by

$$|\psi(t)\rangle=T(t,0)\,|\psi_0\rangle\ , \tag{15}$$

where $T(t,0)$ the unitary time-translation operator satisfying

$$i\hbar\frac{\partial}{\partial t}T(t,0)=HT(t,0)\,,\qquad T(0,0)=1\ , \tag{16}$$

so that

$$T(t,0)=e^{-(i/\hbar)Ht}\ . \tag{17}$$

To obtain information about the time evolution of the system and the physical interpretation of the quantities involved, it is sufficient to evaluate the amplitude

$$\langle\psi(t)\,|\,\psi_0\rangle=\langle\psi_0\,|\,T(t,0)\,|\,\psi_0\rangle\ .$$

Define two resolvent operators for E complex:

$$R(E)=1/(E-H)\ ,\quad R_0(E)=1/(E-H_0')\ . \tag{18}$$

Within a given symmetry, $R(E)$ is given by

$$R(E)=\sum_K\frac{|\phi_K\rangle\langle\phi_K|}{E-E_K}+\int_0^\infty\frac{|\phi_{E'}\rangle\langle\phi_{E'}|}{E-E'}\,dE'\ , \tag{19}$$

where $|\phi_K\rangle$, $|\phi_E\rangle$ are the discrete and continuum states of H with real eigenvalues. $R(E)$ is analytic in the complex E plane except at the poles corresponding to the discrete eigenvalues $E_K<0$ and along the cut for $0<E<\infty$. It is easy to show then that

$$\oint R(E)\,dE=2\pi i \tag{20}$$

and that a function of H can be expressed as

$$f(H)=(1/2\pi i)\oint R(E)f(E)\,dE\ , \tag{21}$$

where the path of integration is closed around the whole real E axis in the positive direction. One thus has

$$T(t,0)=e^{-(i/\hbar)Ht}=(1/2\pi i)\oint R(E)\,e^{-(i/\hbar)Et}\,dE\ , \tag{22}$$

and $R(E)$ may be taken to have the physical meaning of an energy distribution density. To evaluate Eq. (22) I express $R(E)$ in terms of $R_0(E)$ and V:

$$R(E)=R_0(E)+R_0(E)\,VR_0(E)+R_0(E)\,VR_0(E)VR(E) \tag{23}$$

or, since

$$\begin{aligned}&\langle\psi_0\,|R_0(E)VR_0(E)|\,\psi_0\rangle=0,\\ &R(E)=1/[E-H_0-VR_0(E)V]\ .\end{aligned} \tag{24}$$

The quantity $\langle\psi_0|\,VR_0(E)V\,|\psi_0\rangle$ is complex and can be written as

$$\langle\psi_0|\,VR_0(E)V\,|\psi_0\rangle=\Delta(E)-\tfrac{1}{2}i\,\Gamma(E)\ , \tag{25}$$

where the negative sign assures that for $t>0$ the integral (22) converges. I then obtain, for $t>0$

$$\langle\psi_0|\,T(t,0)\,|\psi_0\rangle=\frac{1}{2\pi i}\int_{-\infty-i\epsilon}^{+\infty-i\epsilon}\frac{e^{-(i/\hbar)Et}\,dE}{E-E_0-\Delta(E)+\frac{1}{2}i\,\Gamma(E)}\ , \tag{26}$$

where ϵ is infinitesimal. Assuming that the quantities $\Delta(E)$ and $\Gamma(E)$ are very small compared to E_0 and essentially independent of energy, we may expand them in series around E_0 to obtain $\Delta(E)=\Delta(E_0)$ and $\Gamma(E)=\Gamma(E_0)$. The integral of Eq. (26) can then be evaluated by a simple contour integration in the lower-half E plane with the result

$$\langle\psi_0|\,T(t,0)\,|\psi_0\rangle = e^{-(i/\hbar)[E_0+\Delta(E_0)]t}\,e^{-(1/2\hbar)\Gamma(E_0)t} . \tag{27}$$

Equation (27) has the correct limiting values for $t\to 0$ or $t\to\infty$. Furthermore, it provides the basis for the physical interpretation of the quantities $\Delta(E_0)$ and $\Gamma(E_0)$ which now are seen to represent the energy shift and the inverse of the lifetime $\tau = (\hbar/\Gamma)$, respectively. They are given explicitly in terms of matrix elements by separating the operator $VR_0(E)V$ into its Hermitian and skew-Hermitian parts so that from Eq. (25):

$$\Delta(E_0) = \langle\psi_0|\,V\frac{\mathcal{P}}{E_0 - H_0'}V\,|\psi_0\rangle , \tag{28}$$

where $\mathcal{P}$ denotes the Cauchy principal value, and

$$\Gamma(E_0) = 2\pi\langle\psi_0\,|V\delta(E_0 - H_0')\,V|\,\psi_0\rangle . \tag{29}$$

Using Eqs. (9) and (12), Eq. (29) can finally be cast into the familiar Golden-Rule formula

$$\Gamma(E_0) = 2\pi|\,\langle\psi_0|H|\,U(E_0,\alpha)\rangle|^2\rho_U(E_0) , \tag{30}$$

where the density $\rho_U(E_0)$ is unit if the asymptotic normalization of Eqs. (13) and (14) is adopted.

The quantities $\Delta(E_0)$ and $\Gamma(E_0)$ are defined uniquely by Eqs. (28) and (30) in terms of matrix elements of the wave functions $\psi_0(\vec{r})$ and $U_{E_0,\alpha}(\vec{r})$, exact solutions of the eigenvalue equations (3) and (9) under specified boundary conditions. Experimental and theoretical results suggest that both are very small. This fact justifies completely a theoretical approach which predicts E_0 instead of E since, given the inaccuracies of the calculation, the two energies are the same for all practical purposes. Furthermore, the smallness of Γ is a prerequisite for the "localized state with a square-integrable wave-function" point of view since the larger Γ is, the less physical significance $|\psi_0\rangle$ has. With the above in mind, it seems sufficient to know a good approximation to $|\psi_0\rangle$, E_0, and $|U(E_0,\alpha)\rangle$ in order to predict the observable quantities E and Γ of a many-electron system with reasonable accuracy. This of course requires the solution of an N-body problem for both $\psi_0(\vec{r})$ and $U(\vec{r}, E_0, \alpha)$. The methods for solution of the scattering state problem are rather incomplete at present since no approach exists which accurately accounts for all correlation and polarization effects. Miller[66,77] however has suggested that for Eq. (30) even an approximate continuum wave function can yield good results. His calculations on He as well as those of Bhatia and Temkin[56] who used three types of final-state wave functions of different accuracy with very similar results for Γ, support this suggestion. However, Miller's encouraging idea has thus far been tested only for the relatively simple ($2s\,2p\;{}^1P^0 \to 1skp\;{}^1P^0$) two-electron case and it remains to be seen to what extent it is applicable for an arbitrary N-electron system. Nevertheless, in this work I will assume that $\Gamma(E_0)$ of Eq. (30) *can* be given accurately with an approximate continuum N-electron wave function easily obtainable (e.g., continuum HF or slightly better), and so the emphasis is put on obtaining accurate $|\psi_0\rangle$ and E_0 which Sec. III B deals with.

B. Calculation of the Energy of an Autoionizing State of a Many-Electron Atom From a Variational Principle

I am interested in calculating the energy E_0^a of the autoionizing state[78] $|\psi_0^a\rangle$ by the application of a variational method which should have the extremely useful and necessary property of "upper boundness" to ensure convergence to the exact E_0^a for arbitrary variations of a trial function $\tilde{\psi}_0^a(\vec{r})$. The mathematical problem facing us is the existence of an infinity of lower-lying states belonging to the same symmetry as $|\psi_0^a\rangle$. A valid variational method should include conditions under which the function space of these states is projected out. One sees that the application of the O'Malley-Geltman variational principle is possible only for two-electron systems as these authors have shown by their special choice of the projectors P and Q. On the other hand, the rigorous application of the theorems by Hylleraas, Undheim, and McDonald[79] (HUM) and Sinanoğlu[80] developed for arbitrary N-electron discrete states, is also impossible since they require the consideration of the exact number of lower-state wave functions. Here I will show that an upper bound to second order in energy is indeed possible by the application of certain easily attained restrictions. The method is rather general and, with suitable modifications, applicable, e.g., to ordinary excited-state second-order property calculations. It might also prove useful for certain scattering problems where the upper-bound property to the phase shift is impossible to prove due to the infinity of unknown lower-states wave functions.[81]

From Eq. (3), I want to solve for a trial function $\tilde{\psi}_0^a(\vec{r})$ of energy $\tilde{E}_0^a$ satisfying

$$\lim_{\tilde{\psi}_0^a\to\psi_0^a}\tilde{E}_0^a = \lim_{\tilde{\psi}_0^a\to\psi_0^a}\frac{\langle\tilde{\psi}_0^a|H|\tilde{\psi}_0^a\rangle}{\langle\tilde{\psi}_0^a|\tilde{\psi}_0^a\rangle} \geqslant E_0^a = \frac{\langle\psi_0^a|QHQ|\psi_0^a\rangle}{\langle\psi_0^a|\psi_0^a\rangle} , \tag{31}$$

with the boundary condition of square integrability. As is well known, the eigenvalue problem in the Hilbert space of square-integrable functions is equivalent to solving an Euler variational equation:

$$\delta\tilde{E}\,[\tilde{\psi}_0^a] = \delta\left(\frac{\langle\tilde{\psi}_0^a|H|\tilde{\psi}_0^a\rangle}{\langle\tilde{\psi}_0^a|\tilde{\psi}_0^a\rangle}\right) = 0 . \tag{32}$$

As in the case of ordinary, discrete states, I assume that there is a direct one to-one correspondence between physical reality and the central field approximation. This implies that a first approximation to an autoionizing state can be written as a configuration in terms of orbitals and total angular momentum quantum numbers under the physical restrictions that energy and symmetry considerations allow the decay into the continuum of an ion and a free electron. Let the total Hamiltonian operator in the subspace of square-integrable functions be split into

$$H = \mathcal{H}_0 + \mathcal{V} \ , \qquad (33)$$

where $\mathcal{H}_0$ is a separable (sum of one-particle Hamiltonians) operator having as solutions orbital approximation wave functions assumed known. In particular

$$\mathcal{H}_0 | \phi_0^a \rangle = \epsilon_0^a | \phi_0^a \rangle \, , \qquad (34)$$

where $\phi_0^a(\vec{r})$ is the "independent-particle approximation" wave function corresponding to the configurational assignment of the autoionizing state. Let

$$| \psi_0^a \rangle = | \phi_0^a \rangle + | \chi^a \rangle$$

with (35)

$$\langle \phi_0^a | \chi^a \rangle = 0 \, ;$$

one may then write

$$| \tilde{\psi}_0^a \rangle = | \psi_0^a \rangle + | \delta\psi_0^a \rangle = | \psi_0^a \rangle + | \delta\chi^a \rangle \, . \qquad (36)$$

Consider the functional

$$\langle H - E_0^a \rangle = \frac{\langle \tilde{\psi}_0^a | (H - E_0^a) | \tilde{\psi}_0^a \rangle}{\langle \tilde{\psi}_0^a | \tilde{\psi}_0^a \rangle} = \frac{\langle \delta\chi^a | (H - E_0^a) | \delta\chi^a \rangle}{\langle \tilde{\psi}_0^a | \tilde{\psi}_0^a \rangle} \, ; \qquad (37)$$

then

$$\tilde{E}_0^a [\tilde{\psi}_0^a] = E_0^a + \frac{\langle \delta\chi^a | (H - E_0^a) | \delta\chi^a \rangle}{\langle \tilde{\psi}_0^a | \tilde{\psi}_0^a \rangle} \, , \qquad (38)$$

and if $E_0^a = \epsilon_0^a + \delta E^a$, Eq. (38) takes the form

$$\tilde{E}_0^a [\tilde{\psi}_0^a] = E_0^a + \frac{\langle \delta\chi^a | (\mathcal{H}_0 - \epsilon_0^a) | \delta\chi^a \rangle}{\langle \tilde{\psi}_0^a | \tilde{\psi}_0^a \rangle} + \frac{\langle \delta\chi^a | (\mathcal{V} - \delta E^a) | \delta\chi^a \rangle}{\langle \tilde{\psi}_0^a | \tilde{\psi}_0^a \rangle} \, . \qquad (39)$$

The last term of Eq. (39), representing third- and higher-order corrections, is extremely small and negligible, especially when $\phi_0^a(\vec{r})$ is the Hartree-Fock solution. I then consider only the second term and from the spectral resolution of the operator $(\mathcal{H}_0 - \epsilon_0^a)$ I obtain (omitting $\langle \tilde{\psi}_0^a | \tilde{\psi}_0^a \rangle$)

$$\tilde{E}_0^a [\tilde{\psi}_0^a] \approx E_0^a + \mathbf{S}_{n=-\infty}^{\mathrm{lim} E_0^a} (\epsilon_0^n - \epsilon_0^a) | \langle \phi_0^n | \delta\chi^a \rangle |^2 + \mathbf{S}^{\infty}_{m = \mathrm{lim} E_0^a} (\epsilon_0^m - \epsilon_0^a) | \langle \phi_0^m | \delta\chi^a \rangle |^2 \, , \qquad (40)$$

where **S** implies summation over discrete and integration over continuum states. The index n in the zeroth-order N-particle kets $| \phi_0^n \rangle$ represents the configuration of the states of same symmetry but of lower energy than E_0^a.

The configuration corresponding to the autoionizing state $| \psi_a^0 \rangle$ is usually singly or doubly excited. The spin orbitals entering $| \phi_0^a \rangle$ and $| \phi_0^n \rangle$ can be created from local or nonlocal potentials. Functions obtained from a local potential (e.g., Hartree-Fock-Slater) are not too convenient as a starting point for improvement to account for the error $| \chi^a \rangle$ or δE^a—although they are perfectly good for the variational principle derived below. Hence, I concentrate on the "best"—from the energy point of view—zeroth-order function, the Hartree-Fock.

There are two physically and mathematically meaningful ways by which the N-electron functions $\phi_0^n(\vec{r})$ can be obtained: (a) The spin orbitals entering $\phi_0^n(\vec{r})$ are calculated from a V^{N-1} potential, constructed from the orbitals of $\phi_0^a(\vec{r})$ and preserving the physical correspondence as suggested by Kelly[82] and Silverstone and Yin.[83] The $\phi_0^n(\vec{r})$ then should really be written as $\phi_0^{n(a)}(\vec{r})$. However, such a procedure for constructing the $\phi_0^n(\vec{r})$ renders them, strictly speaking, only approximate eigenfunctions of the Hartree-Fock (HF) operator $\mathcal{H}_0$ since the self-consistency of the problem—particular to the HF operator which is defined in terms of the orbital approximation N-electron function to which it is applied—is neglected. I.e., $\mathcal{H}_0 | \phi_0^{n(a)} \rangle \neq \epsilon_0^n | \phi_0^{n(a)} \rangle$ if the orbitals entering $| \phi_0^{n(a)} \rangle$ are constructed from a V^{N-1} potential from the term $| \phi_0^a \rangle$, and ϵ_0^n, the true HF eigenvalue of the term that $| \phi_0^n \rangle$ describes. (b) Each $\phi_0^n(\vec{r})$ is constructed from spin orbitals obtained self-consistently for each state separately. Now each $\phi_0^n(\vec{r})$ is an eigenfunction of $\mathcal{H}_0$. Here it should be made clear that $\mathcal{H}_0$, as an operator, signifies a prescription on how to construct an eigenvalue equation and is thus unique, although in its actual application it becomes state dependent unlike the operator of the first category which remains fixed for a given set of orbitals. The spectrum $\{\epsilon_0^n\}$ of the self-consistently computed $\phi_0^n(\vec{r})$ resembles the true spectrum very closely. In cases where the individual spin orbitals for different states belong to the same irreducible representation of $O(3) \otimes SU_2$ (e.g., Rydberg states) the functions $\phi_0^n(\vec{r})$ are orthogonal to about 10^{-4}.[84] Otherwise, they are exactly orthogonal on account of the orthogonality of the spherical harmonics of the different orbitals. The resolution of the identity in Eq. (40) can thus be achieved well in terms of the eigenfunctions of this category.

Now suppose I consider the $\phi_0^a(\vec{r})$ Hartree-Fock function. Such a function can be obtained, for example analytically, by the Roothaan restricted Hartree-Fock method[85] but not too easily since often convergence is not as good for a "diffuse" autoionizing state as it is for ordinary ground states. It can be argued[86] that in most cases its energy satisfies the upper-bound property without explicit orthogonalization to lower states. Essentially the proper roots (optimized with respect to linear and nonlinear parameters) are found from the correct physical restrictions and occupancy, vector coupling coefficients, number of nodes of radial functions and $O(3) \otimes SU_2$ symmetry for each orbital, in addition to good initial estimates of the radial functions. There are a few cases however where the HF function for a single configuration may lie below the true energy corresponding to the actual state. These are cases where near-degeneracy configurations become equivalent and the proper zeroth-order state should really be a linear combination of HF functions corresponding to the degenerate configurations (e.g., the $2s3p \pm 3s2p\ {}^1P^0$ states[87]).

The HF function is in general given as a linear combination of Slater determinants belonging to the same configuration. For purposes of demonstration, below I represent them by single N-electron kets containing HF spin orbitals.

For a singly excited state we may write

$$\phi_0^a(\vec{r}) = |K_1^a(\vec{r}_1) K_2^a(\vec{r}_2) \cdots K_{(N+1)_j}^a(\vec{r}_N)\rangle , \tag{41}$$

where K_1^a, $K_2^a \cdots$ are HF spin orbitals ($1s\alpha$, $1s\beta\cdots$) and the subscript $(N+1)_j$ indicates that an inner electron, initially occupying spin orbital j, has been placed in a spin orbital outside the ground-state configurational assignment. Similarly, for a doubly excited state

$$\phi_0^a(\vec{r}) = |K_1^a(\vec{r}_1) K_2^a(\vec{r}_2) \cdots K_{(N+1)_i}^a(\vec{r}_{N-1}) K_{(N+2)_j}^a(\vec{r}_N)\rangle . \tag{42}$$

For any $\phi_0^n(\vec{r})$ below $\phi_0^a(\vec{r})$ having the same symmetry we have

$$\phi_0^n(\vec{r}) = |K_1^n(\vec{r}_1) K_2^n(\vec{r}_2) \cdots K_{N-1}^n(\vec{r}_{N-1}) K_q^n(\vec{r}_N)\rangle , \tag{43}$$

where K_{N-1}^n is the last orbital of the ionic core and K_q^n may range from the last ground-state spin orbital to the Rydberg-series limit, to a continuum orbital. The symmetries of the individual orbitals K_{N-1}^n and K_q^n depend on the open channels accessible for decay.

It is obvious that K_q^n is different for every $\phi_0^n(\vec{r})$. The “core orbitals however, $K_1^n \cdots K_{N-1}^n$ may be taken to be invariant for all configurations $\{n\}$, for a given Z, N, and symmetry. (Only the last orbital K_{N-1}^n may be a little changed for certain low Rydberg states due to the separate optimization of each ϕ_0^n). For example, a $(1s^2 2s^2 2p)$ core of a $1s^2 2s^2 2p 3p$ configuration is almost identical to the core of $1s^2 2s^2 2p np$ where $n = 4, 5, 6, \cdots$. This realization forms the basis for the derivation of our variational principle. Because now I may demand that the variations in our trial function should be carried out under the general restriction that

$$\begin{aligned} G(\vec{r}_N) \equiv \int d\vec{r}_1 \cdots d\vec{r}_{N-1} \\ \times \{\mathcal{A}_{N-1}[K_1(\vec{r}_1) \cdots K_{N-1}(\vec{r}_{N-1}))]\} \delta\chi^a(\vec{r}_1 \cdots \vec{r}_N) \\ = 0 . \end{aligned} \tag{44}$$

$K_1 \cdots K_{N-1}$ are the “core” orbitals chosen judiciously from the physics of the problem and $\mathcal{A}_{N-1}$ the many-electron antisymmetrizer. Then, any zeroth-order state containing the “core” one-electron functions will automatically be orthogonal to the trial function $\tilde{\chi}^a(\vec{r})$. Thus all the lower-state negative-energy contributions in Eq. (40) will vanish and an upper bound at least up to second order in energy will be ensured, i.e., $\tilde{E}_0^a[\tilde{\psi}_0^a] > E_0^a$ if Eq. (44) is fulfilled and $\tilde{\psi}_0^a(\vec{r})$, square integrable.

More specifically, consider the following: Let us assume that the nonstationary state is doubly excited (e.g., $\mathrm{Li}^- 1s^2 2p^2\ {}^1S$). Denote it by $|1s \cdots (ml)^2\rangle$. The lower states will be of the form:

$$|(1s \cdots nl)\, n'(\epsilon)\, l'\rangle \quad \text{(core)} ,$$

where

$$n = 1, 2 \cdots , \quad n' = 2, 3, 4, \cdots , \quad l, l' = 0, 1, \cdots , \quad .$$

$|nl\rangle$ is the last occupied orbital $[\equiv K_{N-1}(\vec{r})]$ before the Rydberg (continuum) orbital $|n'(\epsilon)l'\rangle$ $[\equiv K_q(\vec{r}_N)]$. For negative ions, $|n'(\epsilon)l'\rangle$ lie only in the continuum, functions of the continuum parameter ϵ. For demonstration purposes, I consider only two-particle virtual excitations, which contribute to the energy the most. When the electrons in the core orbitals $|1s\rangle$ correlate and are virtually excited to a pair function $u^a(\vec{r}_1, \vec{r}_2)$, then, due to the orthogonality of $u^a(\vec{r}_1, \vec{r}_2)$ to the $|1s\rangle$ function, [Eq. (35)] that part of $\tilde{\chi}^a(\vec{r}_1 \cdots \vec{r}_N)$ containing $u^a(\vec{r}_1, \vec{r}_2)$ will automatically be orthogonal to all lower states containing the $|1s\rangle$ orbital. A similar argument holds for the other core orbitals of the doubly excited state until we reach $|(ml)^2\rangle$, (or intershell correlations involving one ml orbital, which, however, in this case are small). If all the other core orbitals are the same for the autoionizing state and all the lower terms (e.g., the $1s^2$ core in the $1s^2 2p^2\ {}^1S$ case) it is the remaining orbitals $|nl\rangle$ and $|n'(\epsilon)l'\rangle$ that give rise to the infinity of lower states. In order then to guarantee an upper bound to the energy, the variational optimization of the correlation functions $u(\vec{r}_1, \vec{r}_2)$ describing the correlation in $|(ml)^2\rangle$ should be carried out under the restrictions that

$$\begin{aligned} g(\vec{r}_1) = g(\vec{r}_2) = \int d\vec{r}_2 u(\vec{r}_1, \vec{r}_2) nl(\vec{r}_2) \\ = \int d\vec{r}_1 u(\vec{r}_1, \vec{r}_2) nl(\vec{r}_1) = 0 . \end{aligned} \tag{45}$$

In case that $u(\vec{r}_1, \vec{r}_2)$ is expanded in a set of one-electron functions having different symmetry than l, condition (45) is automatically satisfied. Otherwise, Eq. (45) implies a Schmidt orthogonalization. Here I should repeat that the radial part of $|nl\rangle$ is assumed the same for all zeroth-order Rydberg states, which is a very good approximation. If more accuracy is required, especially for systems with a small number of electrons where the charge distribution is more sensitive to configuration, the "core" orbitals may be chosen to be those of the ground state and of the first one or two Rydberg states. Finally, if more than one channel is open, Eq. (45) should be satisfied for each $|nl\rangle$ of the open channels (in reality, not more than two or three in most cases).

C. Applications

The great advantage of this method [Eqs. (31) – (45)] is of course that, through Eqs. (44) and (45), one needs to project onto known one-electron zeroth-order functions to avoid a variational collapse. For orbitals of the inner part of the "core," this is satisfied automatically by virtue of Eq. (35). Otherwise, the variation should be carried out under the constraints of Eq. (45), i.e., orthogonality to $|nl\rangle$. In other words, the Q projection operator of the Feshbach formalism as adopted by O'Malley and Geltman,[54] may now be replaced by $q = 1 - |nl\rangle\langle nl|$, where $|nl\rangle\langle nl|$ is of zeroth order and known for an arbitrary N-electron system. The application of q on variational correlation functions accounting for correlation of valence electrons of the autoionizing state then guarantees an upper bound to the total energy.

In the non-closed-shell many-electron theory (NCSMET) of Silverstone and Sinanoğlu,[26] the correlations in open-shell states are divided into internal, semi-internal, and external. For pair correlations, they describe the following virtual processes: (a) internal: $(i,j) \rightarrow (K,l)$, where (i,j) are occupied HF orbitals and (K,l) are "HF sea" orbitals; (b) semi-internal: $(i,j) \rightarrow (K,\hat{f}_{ij;K})$, where $\hat{f}_{ij;K}(\vec{r}_1)$ is a one-electron function; (c) external: $(i,j) \rightarrow \hat{u}_{ij}(\vec{r}_1,\vec{r}_2)$. The problem of the choice of "HF sea" orbitals for hole states is discussed in Ref. 46.

The internal and semi-internal correlations together are uncoupled from the external to a very good degree of accuracy.[88] In this example, one may then separate the correlation of the $(ml)^2$ pair of electrons of the doubly excited state into (a): $(ml)^2 \rightarrow (K,\hat{f})$ and (b): $(ml)^2 \rightarrow \hat{u}(\vec{r}_1,\vec{r}_2)$. There are two ways to proceed from here. One is to consider suitably parametrized functions for $K(\vec{r})$, $\hat{f}(\vec{r})$, and $u(\vec{r}_1,\vec{r}_2)$ and vary them to minimize the energy under the restrictions that $\langle K|nl\rangle = \langle f|nl\rangle = \langle u|nl\rangle = 0$. An upper bound is obtained but the convergence is slow since some important particle-hole interactions are left out. The other is to consider (a) and (b) separately. First take $|K\rangle = |nl\rangle$. The exact $\hat{f}$ may be written as an expansion in terms of the set of Rydberg and continuum HF orbitals $n'(\epsilon)l'$, i.e.,

$$\begin{aligned}\hat{f} &= \mathbf{S}_{n',\epsilon}\, a_{n'}(\epsilon)\,|n'(\epsilon)l\rangle \\ &= \hat{f}_{\text{discrete}} + \hat{f}_{\text{continuum}}\,,\end{aligned} \tag{46}$$

where $\mathbf{S}$ means summation over discrete and integration over continuum orbitals whose separate contribution to $\hat{f}$ is indicated by the functions $\hat{f}_{\text{disc}}$ and $\hat{f}_{\text{cont}}$. The variational $\tilde{f}$ may be expanded in a suitably parametrized basis (e.g., Slater-type orbitals). Together with the Hartree–Fock and the other internal and semi-internal functions they form a set of one-electron functions which in turn make up the set of N-electron Hartree–Fock and correlation vectors. The variational problem is then "reduced" to an iterative diagonalization procedure of the matrix Hamiltonian in the $\mathcal{L}^2$ function, "nondynamical correlation,"[46] subspace. Optimization of the parameters in the $\tilde{f}$ function to minimize the energy is equivalent to variation of the linear parameters $a_n(\epsilon)$ of Eq. (46), to account for the contribution of the one-electron functions $|n(\epsilon)l\rangle$ to $\hat{f}$. The final vector corresponding to the autoionizing state and its energy, which is still an upper bound by virtue of the separation of the eigenvalues,[46] is found from the iteratively diagonalized matrix by searching for the root for which

$$\langle \tilde{\chi}^a_{\text{corr}} | \tilde{\chi}^a_{\text{corr}} \rangle = \text{minimum}\,,$$

so that (47)

$$\tilde{\psi}^a_0\,(\text{appr}) = \phi^a_{\text{RHF}} + \tilde{\chi}^a\,(\text{appr}).$$

Finally, to the approximate vector $\tilde{\psi}^a_0$ (appr) and its energy we now have to add the external pair function $u(\vec{r}_1,\vec{r}_2)$ of (b) whose optimization must again be subject to the conditions of Eq. (45).

Although I have chosen a doubly excited state as an example, it is obvious that this variational upper-bound method is quite general. In fact, for most inner-hole states, with, say, $1s$ electron missing, (e.g., Li $1s2s^2\,{}^2S$, Ne II $1s2s^22p^6\,{}^2S$) the orthogonality constraints of Eqs. (44) and (45) are automatically satisfied (to a good approximation) due to Eq. (35). Take, for example, the Li $1s2s^2$ ${}^2S$ state. The lower states of ${}^2S$ symmetry have the form $1s^2n(\epsilon)s\;{}^2S$. A pair correlation function orthogonal to the HF $1s$ or $2s$ orbitals of the $1s2s^2$ ${}^2S$ state [Eq. (35)] will also be orthogonal (to a good approximation) to the $1s$ orbital of the $1s^2n(\epsilon)s\;{}^2S$ zeroth-order states.

Parenthetically, I note that the above considerations apply equally well to ordinary discrete states having a finite number of lower states of the same symmetry (e.g., B I $1s\,{}^22s2p\,{}^2S$). Such states have been examined from a many-body point of view by us elsewhere,[25,46] and their radiative transition probabilities to lower-lying states have been calculated. Variational calculations of highly excited discrete states could be justified by invoking the Hylleraas–Undheim–MacDonald theorem which says that if the Hamiltonian is diagonalized within a basis set of dimension M belonging to a given symmetry, the resultant M eigenvalues are upper bounds to the first M real energies of that symmetry. In practice, however, it is not easy to satisfy the requirement of including approximate wave functions for all the lower states of the same symmetry. The present development bypasses this disadvantage and renders N-body variational calculations of discrete highly excited states conceptually rather straightforwardly.

The above variational methods are being applied to a few autoionizing states of atoms and ions with three to nine electrons covering different energy region. For three- and four-electron systems, the "external" energies are computed in an *ab initio* way. For larger atoms they are calculated semiempirically using Sinanoğlu's theory.[26] Only one- and two-particle correlations are considered. However, for negative-ion "compound" states, three-particle correlations may also be somewhat important. The wave functions for such states are fairly "large," extending over a large region of configuration space while at the same time the nuclear "well" is rather small. Roughly speaking then, the electrons would tend to be less localized, and relatively long-range Coulomb forces may contribute here more than in ordinary ground states where pairwise "collisions" due to the short-range "fluctuation potential"[89] dominate the interactions completely.

The details of my calculations and results will be reported elsewhere as soon as they are considered final. Here I give only a few energy positions of "nonstationary" states, prelininary results of many-body calculations. I have found the He$^-$ $2s^2 2p\ ^2P$ and $2s2p^2\ ^2D$ resonances to lie at about 57.3 and 58.4 eV above the ground state, respectively, in good agreement with the scattering experiments[5] which give 57.2 and 58.3 eV, respectively. Furthermore, I predict structure in the scattering or photoionization cross sections for Li I at about 140.7 eV above the ground state (a $^2P^0$ state), for C IV at about 306.7 eV, (a ^2D state) for N I at about 14.9 eV (a ^2D state), and for F I at about 22.4 eV above the ground state (a ^2S state). These states could in principle be observed in particle-atom (ion) scattering experiments or through photon absorption from terms of the ground configurations, and there is obviously a need for their experimental verification.

Finally I report a rather general feature of such state deduced from preliminary calculations. Although in the expansion of the total wave function of a given term the HF function together with the internal part still carry the largest coefficients, certain "semi-internal" correlations now acquire an unusually heavy weight. By considerably "diluting" the HF component, such correlations affect the energy and especially the oscillator strengths from the ground states—when symmetry allows—immensely. For example, the oscillator strength for the N I $1s^2 2s^2 2p^3\ ^2P^0 \rightarrow {}^2D$ transition is reduced from $f = 0.15$, which is the HF value, to $f = 0.004$, when electron correlation in ground and excited states is included. In configuration-interaction language, some of these correlations correspond to configurations Cooper and LaVilla[90] have suggested would affect the intensities of Auger spectra in argon. For example, consider the singly excited F I $1s^2 2s\, 2p^6\ ^2S$ state. For this term we find that "processes" of the type $(i,j) \rightarrow (K,\tilde{f})$, where (i,j,K) Hartree–Fock spin orbitals with (s,p,p) angular symmetry and $\tilde{f}(r)$ a parametrized one-electron function, contribute heavily to the overall charge distribution. These "processes" give rise to "configurations" like $1s^2 2s^2 2p^4 \tilde{f}_s\ ^2S$ and $1s^2 2s^2 2p^4 \tilde{f}_d\ ^2S$, with $\tilde{f}_s$, $\tilde{f}_d$ one-electron functions of s and d symmetry, which are analogous to the configurations Cooper and LaVilla considered for the $3s3p^6\ ^2S$ case. The same, of course, holds for a doubly excited state. For instance, in Li$^-$ $1s^2 2p^2\ {}^{(2S+1)}L$, "configurations" of the type $1s^2 2sf_l(\vec{r})$, ${}^{(2S+1)}L$ are important. The HF transition probability [Eq. (30) with HF wave functions] for a particular open channel may then be altered significantly due to simple matrix elements of the type e.g.,

$$\langle a|1s^2 2p^2\ {}^{(2S+1)}L\rangle + b|1s^2 2s\tilde{f}_l\ {}^{(2S+1)}L\rangle\,|H|\,1s^2 2s\epsilon l\,{}^{(2S+1)}L\rangle\,,$$

where a and b are interaction coefficients and $|\epsilon l\rangle$ is a continuum function of l symmetry.

IV. SYNOPSIS

In this paper I have adopted a "decaying-state" point of view for the description of autoionizing states of an arbitrary N-electron atom. Application of the general theory of damping[75,76] yields the observable quantities, the position and the width. The identification of the inverse of Γ with the lifetime of an exponentially decaying state, as in the case of radiative transitions, is made under the assumption that Γ is small and essentially energy independent. For broad-shape resonances this assumption may not hold and correspondence with a simple exponential decay could be meaningless. I do not attempt to solve for the unnormalizable resonant wave function $\psi(\vec{r})$. Instead, I consider the iterative-variational solution of an eigenvalue equation which the square-integrable wave function $\psi_0^a(\vec{r})$, describing the initial localized state, satisfies. A general variational upper-bound principle in the Hilbert space of square-integrable functions, readily applicable to an arbitrary N-electron excited state, is then derived. The present approach treats all "nonstationary" states, i.e., states observable through electron emission, on an equal basis. In particular, for processes involving the outer electrons, it is complementary to scattering-state approaches like the close-coupling approximation. Preliminary calculations yield the positions of "nonstationary" states in He$^-$ ($2s^2 2p\ ^2P^0$ and $2s2p^2\ ^2D$ at 57.3 and 58.4 eV, respectively), in Li I ($^2P^0$ at 140.7 eV), in C IV (^2D at 306.7 eV), in N I(^2D at 14.9 eV), in F I (^2S at 22.4 eV) as well as in other atoms and ions. Finally, I recall that the knowledge of $|\psi_0^a\rangle$ and E_0^a is essential to an approximate theoretical construction of photon-absorption spectra from a ground state $|\psi_G\rangle$. When the problem of the continuum N-electron wave function is well understood, so that accurate evaluation of the matrix elements $\langle\psi_G|\vec{D}|\psi_0^a\rangle$ (a measure of the excess transition probability[16,91]), $\langle\psi_G|\vec{D}|U_0(E,\alpha)\rangle$, and $\langle\psi_0^a|H|U_0(E_0^a, \alpha\rangle$ is possible, where $\vec{D}$ is the dipole operator, the absorption spectrum for an N-electron system over a specified energy region could be estimated rather well using assumptions and methods developed for bound-bound transition probabilities.[92,25]

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APPENDIX: A HEURISTIC ARGUMENT ON THE MAGNITUDE OF THE LEVEL SHIFT Δ

The energy at which the "nonstationary" states are observed is E of Eq. (1) (real part) and not E_0^a of Eq. (3).[78] The difference $\Delta = E - E_0^a$ may be called the "level shift" and in this work it is uniquely defined. It is given exactly by Eq. (28). Physical evidence suggests that Δ is very small. Similarly, very accurate calculations by Bhatia and Temkin[56] on He, using the P, Q formalism, show that Δ is indeed very small. Therefore, a theoretical calculation of E_0^a is justified since uncertainties intrinsic in the N-body problem are at least of the same order of magnitude as Δ. One could in principle calculate Δ from Eq. (28) for each case. This, however, would be rather cumbersome. To obtain a crude estimate of its magnitude, I consider the following: From Eqs. (1)–(8) one obtains

$$(E - H_0')|P\psi\rangle = V|\psi\rangle - (E - E_0^a)|\psi_0^a\rangle , \tag{A1}$$

with

$$|P\psi\rangle = |\psi\rangle - |\psi_0^a\rangle , \quad \langle\psi|\psi_0^a\rangle = 1 . \tag{A2}$$

Apply P to both sides of Eq. (A1):

$$(E - H_0')|P\psi\rangle = PV|\psi\rangle . \tag{A3}$$

From general considerations of perturbation theory and from the evidence of weak coupling, one may expect that "distant" continuum states $|U(E)\rangle$ do not contribute to the interaction whose largest portion must come from an energy strip around E_0^a. In particular, then, I assume that $|\psi_0^a\rangle$ interacts with continuum states just "next" to it, within an energy interval of Δ (i.e., from $E_0^a - \frac{1}{2}\Delta$ to $E_0^a + \frac{1}{2}\Delta$). The matrix elements of V are assumed finite and constant for $|U(E)\rangle$ in the above energy region and zero otherwise. One may then invert $(E - E_0')$ and solve for $|P\psi\rangle$ approximately. Thus

$$|\psi\rangle = |\psi_0^a\rangle + \frac{1}{E - H_0'} PV|\psi\rangle \tag{A4}$$

and

$$\Delta = E - E_0 \approx \langle\psi_0^a|H \frac{1}{E - PHP} H|\psi_0^a\rangle , \tag{A5}$$

where P now selects only a specific group of continuum states so that

$$|\Delta| \approx \int_{E_0^a - \Delta/2}^{E_0^a + \Delta/2} \frac{|\langle\psi_0^a|H|U(E')\rangle|^2 \rho_U(E')\, dE'}{E - E'} . \tag{A6}$$

Letting $E' = E_0^a + \epsilon$, where ϵ is small and expanding around E_0^a one obtains

$$|\Delta| \approx \ln 3\, |\langle\psi_0^a|H|U(E_0^a)\rangle|^2 \rho_U(E_0^a) \tag{A7}$$

$$\approx [\ln 3/2\pi]\, \Gamma(E_0^a) . \tag{A8}$$

To test (A8), consider two cases in He, the $2s2p\ ^1P^0$ and the $(2s3p + 2p3s)\ ^1P^0$ states, for which accurate experimental results by Madden and Codling[4] and theoretical results by Bhatia and Temkin (BT)[56] and Altick and Moore (AM)[62] exist. The experiment (photon absorption in the uv) yields $\Gamma = 0.038 \pm 0.004$ eV for the $2s2p\ ^1P^0$ term and $\Gamma = 0.008 \pm 0.004$ eV for the $(2s3p + 2p3s)\ ^1P^0$ term. The theoretical results on Δ are evaluated by integrating Eq. (28). They are for $2s2p\ ^1P^0$

$$\Delta = -0.007 \text{ eV (BT)}, \qquad \Delta = -0.009 \text{ eV (AM)},$$

and for $(2s3p + 2p\,3s)\ ^1P^0$

$$\Delta = -0.0021 \text{ eV (BT)}, \quad \Delta = -0.0017 \text{ eV (AM)}.$$

Using Eq. (A8) and the experimental results, I obtain

$$|\Delta| \approx 0.006 \quad \text{for} \quad 2s2p\ ^1P^0,$$

$$|\Delta| \approx 0.0013 \quad \text{for} \quad (2s3p + 2p3s)\ ^1P^0$$

in good agreement with the order of magnitude from direct calculation.

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