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Energies and widths of electron scattering and Auger resonances of atomic beryllium

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The present calculation is the first application of a Green's-function approach to resonance states based upon the direct use of Siegert boundary conditions. Consequently, the emphasis is on methodological aspects rather than the description of a great number of resonances. Of particular interest is the treatment of inner-shell vacancies and their satellites as resonance states. We have evaluated the energies and widths of one electron scattering resonance and three Auger-type resonances all of ^2S symmetry.

I. INTRODUCTION

The recent interest in energies and lifetimes of inner-shell vacancies is partly stimulated by quite a number of heavy-particle collision experiments. Accompanying theoretical calculations, which can account for the positions and intensities of the resulting Auger lines, are expected to provide information about the initial collision process which created the inner-shell vacancies in the first place. Contrary to the situation encountered in the calculation of the energies of ground states and low-lying excited states of atoms and molecules, the methods applied to the energies and lifetimes of inner-shell processes are less developed. It is quite clear that any method based solely on an independent particle model like, e.g., Hartree-Fock (HF) is not adequate for treating a process as complicated as the decay of an inner-shell vacancy although sometimes HF energies are surprisingly good.[1,2] As pointed out by Kelly[3] this may be due to a partial cancellation between relativistic and correlation energy contributions and thus somewhat deceptive. This inadequacy of the HF approach manifests itself more clearly in the results for the Auger intensities which are usually quite poor. Kelly was able, however, to obtain much better agreement with experiment by the inclusion of correlation effects through a lowest-order many-body perturbation theory which, in the particular way it was carried out, included also some higher-order contributions. The source of remaining discrepancies with experimental findings could not, however, be cleared up. It seems quite appropriate therefore to develop many-body methods which go beyond the approximations employed in previous theoretical work.

The present paper is a first application of the method proposed in our companion paper[4] to an inner-shell vacancy of the beryllium atom. Henceforth we will refer to this paper as I, and references made to the equations of the first paper will be denoted by quoting the corresponding equation number preceded by I. The present approach, which to our knowledge is quite novel, consists of an extension of the standard one-particle Green's-function technique (previously successfully applied to the calculation of ionization potentials by Cederbaum and Domcke[5] and electron affinities by Kurtz and Öhrn,[6] for instance) to the treatment of metastable states, namely, Auger type resonances and electron scattering resonances. The necessary analytical continuation of the Dyson equation onto the complex plane is here achieved by very much the same means we chose for the Schrödinger equation in our first paper analyzing the Siegert approach[7] and differs substantially from an alternative method presented by Winkler.[8]

The purpose of the present publication is to demonstrate that we obtain indeed the complex eigenvalues corresponding to both inner-shell vacancies and electron scattering resonances predicted in I. Further, we investigated the dependence of the results on the size of the basis set which consists of Slater-type orbitals (STO) plus one Siegert orbital, the particular form of which is explained in I [see (I-20a) for electron scattering resonances and (I-30) for Auger resonances]. The self-energy operator employed is evaluated in second-order perturbation theory. The effect of the summations to infinite order of certain types of diagrams implicitly brought about by the solution of Dyson's equation has been elucidated by Doll and Reinhardt[9] and seen to be essentially a renormalization of the usual second-order perturbation corrections.

The key quantities evaluated here are energy differences between excited states of an $(N\pm 1)$-electron system and the ground state of the corresponding N-electron system. The excited states for which our method has been designed all lie above the continuum thresholds of the corresponding systems and have therefore a complex energy, the imaginary part of which determines half of the width of the resonance while the real part compares directly to the experimental energy value. It is true, however, that straightforward application of our method in energy regions below the continuum thresholds yields proper ionization potentials and electron affinities as real solutions of Dyson's equation. The same results can, of course, be obtained by intrinsically simpler methods.[5] Nevertheless, this property was a welcome means to check the computations.

II. BASIS SETS

The basis sets used in the present investigation are obtained by augmenting the basis set of Sabelli and Hinze,[10] which has been used also in the work of Doll and Reinhardt.[9] Thus it was possible to check our computer codes (in particular the self-energy part) by simple recalculation of their results for the ionization potentials of Be and He. The exponent of each STO added to the original basis orbitals was determined by the—admittedly rather arbitrary—requirement that the overlap of the new orbital with all the rest of the basis should not exceed 90%.[11] Of the two choices, namely, either to increase or to decrease the magnitude of the exponent starting from a value already present in the basis, we picked the latter. This way we obtained basis sets which tend to accumulate virtual Hartree-Fock-Roothaan (HFR) orbital energies in the low-energy region. Owing to the lack of a minimal energy priciple for the type of excited states we are calculating here, this feature provides some *a priori* justification for our selection priciple.

The data on the basis parameters are collected in Table I. In the course of this work we frequently refer to a particular basis by a combination of three numbers, e.g., l-m-n, referring by this to a basis consisting of the first l s-orbitals, the first m p-orbitals and the first n d-orbitals of those given in Table I. The radial functions of the STO's are given by

$$R_{nl}(r)=\left(\frac{(2\zeta)^{2n+1}}{(2n)!}\right)^{1/2} r^{n-1}e^{-\zeta r}\,. \tag{1}$$

TABLE I. The parameters of the Slater-type orbitals used in the present work.

l	n	ζ
0	1	5.4297
0	1	2.9954
0	2	1.1977
0	2	0.8923
0	3	3.5810
0	1	0.3340
0	1	0.1670
1	2	5.6998
1	2	2.7850
1	3	1.4387
1	3	0.9819
1	4	4.1500
1	2	0.4800
2	3	1.2662
2	3	7.8314

As described in I, for the calculation of resonances, the STO basis has to be augmented by one complex Siegert orbital ϕ_k, the radial part of which is given by

$$\phi_k(r)=[1-\exp(-\beta r^m)]\,\frac{\exp[i(kr-\pi l/2]}{r}\,, \tag{2}$$

with Im$k<0$ for resonances of both kinds. The parameter m will be discussed below. This form corresponds to the approximation employed previously by Miller and co-workers.[12] The reader is referred to I for further details. For resonances of the negative ion the relation between the complex wave number k and the energy parameter ϵ of the Green's function is given by

$$k={}_{+}\sqrt{2\epsilon}\,, \tag{3}$$

while for positive-ion resonances we have

$$k={}_{+}[2(T_t-\epsilon)]^{1/2}\,, \tag{4}$$

with T_t being the (experimental) two-electron continuum threshold of the neutral system.

III. THE CALCULATION

The calculation proceeds in four major steps: (i) Solution of the HFR equations to obtain a set of occupied and unoccupied HFR orbitals with corresponding energies. (ii) These results are then utilized to set up the self-energy matrix given in (I-25). In this step it has proven to be advantageous to store the necessary two-electron matrix elements in the HFR representation in order to evaluate the self-energy matrix elements for various values of the energy parameter efficiently. Except that the energy parameter is complex, everything so far is the standard Green's-function technique for the calculation of ionization potentials. (iii) The third step consists of the calculation of the borderline matrix elements of the complex matrix given in (I-28). These matrix elements involve the Siegert state explicitly. This step will be commented on below. (iv) Finally, we search for self-consistent eigenvalues of the complex matrix set up in the previous step by repeated diagonalization for various energy values. In this step we utilize a second-order polynomial fit to predict the position of the self-consistent root in the complex energy plane. Usually only a few iterations (often only a single iteration) were sufficient to locate it with reasonable accuracy. But, of course, we had an excellent idea where to initiate the search for Auger resonances. In the last two steps we made use of the HFR orbitals obtained in the beginning in quite another sense, namely, as a basis set (together with the Siegert orbital) for the diagonalization of the Layzer operator given in (I-4).

In the present exploratory investigation we have taken advantage of the convenience of a cut-off function of the simple form

$$f(r) = 1 - \exp(-\beta r)\,, \tag{5}$$

which leads to closed form expressions for all integrals. The linear rise of the Siegert orbital at the origin introduced by the choice $m = 1$ is expected to cause a certain amount of strain on the STO basis in the variational calculation resulting in a noticeable β dependence of the results (at least in connection with the small basis sets used so far) which should be much reduced, however, if a higher power of r in the exponent is used. Since the β dependence is not critical, as will be demonstrated in the next section, we accept some β dependence in order that all two-particle matrix elements containing the Siegert orbital can be evaluated analytically rather than numerically. Owing to the complex nature of the Siegert orbital the corresponding Slater integral $F^{(K)}$ is complex also. The explicit formula is given in the Appendix.

IV. RESULTS

The results of the present investigation are presented in Table II. The dependence of the (self-consistent) resonance eigenvalue on the value of the cut-off parameter β has been investigated in some detail for the case of the first Auger-type resonance at about -125.5 eV. Employing the smallest basis set (5-5-2) for which the dependency is expected to be more pronounced than for larger basis sets, we observe that there exists a relatively broad interval ($10 \lesssim \beta \lesssim 20$) in which the calculated width does not change appreciably. Our findings are presented in Fig. 1. It should be mentioned also that for an (admittedly exaggerated) value of $\beta = 100.0$ the calculated width has shrunk to 0.788×10^{-3} eV. While this behavior finds a simple explanation in the fact that the rapid rise of the Siegert orbital at the origin cannot easily be counter balanced by the rest of the limited basis, one should realize this parameter dependency and make sure that reported results are always taken from a region of stability with respect to changes in β.

TABLE II. Resonance energies of the positive and negative beryllium ion obtained from the 7-6-2 basis set.

Re ϵ (eV)	Im ϵ (eV)
-125.47	0.0102
-137.45	0.00013
-139.98	0.0033
11.72	-0.0142

It is expected that basis set dependence becomes weaker and weaker for larger basis sets. Although our present computational facilities prohibit an exhaustive investigation of this point we are able to demonstrate moderate stability of results for Auger-type resonances even with the two small basis sets employed in the present work. The energy of the first Auger resonance obtained from the 5-5-2 basis is $-125.4764 + i0.0112$ eV, while the value obtained from the larger 7-6-2 basis is $-125.4734 + i0.01024$ eV. The cut-off parameter is $\beta = 10$ in both cases. A similar stability is not expected for electron scattering resonances, since the Sabelli-Hinze basis (i.e., our 5-5-2 basis) being set up for ground-state-energy calculations does not contain orbital exponents appropriate to describe excited orbitals (e.g., $2p$, $3s$, $3d$) of the negative ion. The smallest exponent is $\xi = 0.8923$ in the 5-5-2 basis. Mainly for this obvious deficiency of the 5-5-2 basis we do not report any electron scattering resonances obtained from the smaller basis.

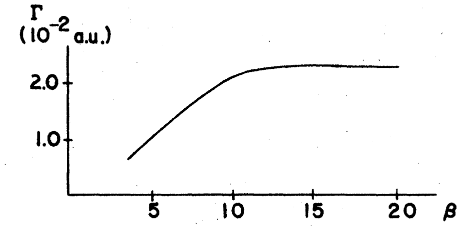

FIG. 1. The dependence of the width of the first Auger-type resonance on the cut-off parameter β. This calculation employed the 5-5-2 basis of Sabelli and Hinze (Ref. 10).

V. DISCUSSION

Since the method employed in the present work is quite different from previous calculations of energies and lifetimes of inner-shell vacancies the comparison to existing results is not straightforward and requires some commentary. To our knowledge there are so far no data on electron scattering resonances of atomic beryllium to compare with. We therefore present our result (the resonance at $11.72 - i0.0142$ eV) merely as one example showing that the formalism is capable of producing resonance solutions corresponding to that particular time ordering of the Green's function. A more detailed study of both the efficiency of different approximations of the self-energy operator and the dependence of basis sets is currently being carried out for systems with more experimental and theoretical data to compare with.

There are, however, some recent measurements of the energies of ^2S Auger resonances of beryllium[13-15] as well as some energy calculations.[16,17] Combining the later measurements[15] with the tentative spectroscopic assignments given in the earlier publication[13] their findings are 123.63 eV ($1s\,2s^2$), 135.10 eV ($1s\,2p^2$), 138.1 eV [$(1s\,2s\,^3S)3s$], and 140.5 eV [$(1s\,2s\,^1S)3s$]. The approximation for the self-energy operator employed in the present work does not allow for orbital relaxation. We attribute most (if not all) of the 1.5% deviation in the ($1s\,2s^2$) energy of our calculation to this deficiency, since otherwise the result is relatively stable, e.g., with respect to an increase of the number of basis orbitals, as pointed out in the previous section. Furthermore, there is no way to obtain the first satellite ($1s\,2p^2$) in the present second-order approximation of the self-energy which allows only for two holes in the intermediate state. It should be mentioned, however, that there are alternative ways, namely, to calculate Auger-type resonances as electron scattering resonances from the doubly ionized system Be^{++}. This approach does allow for the calculation of this particular type of metastable state even with a second-order self-energy. This, however, has not been attempted here. The energies of the other two satellites, 137.45 and 139.98 eV, compare quite favorably to the measured values. The stability of these two results with respect to saturation of the basis has not yet been investigated, since contrary to the case of the ($1s\,2s^2$) resonance it was not possible to obtain these resonances employing the 5-5-2 basis set due to the above mentioned lack of exponents for a reasonable representation of the $3s$ orbital.

The comparison of the obtained widths to the only two experimental numbers known to us of the lowest Auger resonance, namely, the fluorescence yield measurements of Dick and Lucas[18] and Feser[19] is not really possible since the measurements were done on solid beryllium. Even relatively small admixtures of angular momentum $l=1$ in the valence electron wave functions can cause an order of magnitude increase in the flourescence yield ω.[16] Indeed, the observed values of $\omega=3.04\times10^{-4}\pm20\%$ (Dick and Lucas) and $\omega=3.6\times10^{-4}\pm30\%$ (Feser) are larger than the values obtained by both Kelly (2.24×10^{-5}) and the present authors (1.01×10^{-4}) using the radiative decay rates given by Kelly.

It seems therefore more reasonable to compare the theoretical results directly. Kelly's Auger decay rate for the $1s(2s)^2\,^2S$ state (0.34×10^{-2} a.u.) is approximately five times larger than the value for the width Γ of the Auger resonance obtained here (0.753×10^{-3} a.u.) using the 7-6-2 basis. Since our results and those of Kelly are not in agreement, a brief discussion of Kelly's calculational method is in order. Kelly calculated the decay rate by using a "Golden Rule" expression employing a two configuration ($1s2s^2\,^2S$ and $1s\,2p^2\,^2S$) multiconfigurational self-consistent field (MCSCF) wave function as the initial state (which is to account for the $2s$-$2p$ near degeneracy) and a $1s^2\,ks$ HF final state. Fermi's Golden Rule gives the lowest-order term in a perturbational expansion of the decay rate[20] about an uncorrelated model discrete state embedded in a continuum (in an expansion of a complex pole of the resolvent $\epsilon - i\Gamma/2$ about $\Gamma=0$). However, recent calculations[21,22] on autoionizing states of He have shown the simple Golden Rule results to be grossly in error. Furthermore, they found that in general the golden rule predicts too large a rate for electron scattering resonances. This is attributed by these authors to the general rule that second-order perturbation theory usually "overshoots" the correlation contribution since the various correlating motions are uncoupled (remember that it is only the correlation that couples the discrete state with the embedding continuum). Kelly's investigations[3] of K Auger rates for Ne, for which atom detailed experimental data exist,[23] seem to indicate that these conclusions hold for Auger resonances as well as for the He resonances. After inclusion of higher-order corrections, however, Kelly was able to obtain good agreement with experiment. While the present Siegert Green's-function method is intrinsically a more accurate method than Fermi's Golden Rule, it remains to be seen if a better approximation of the self-energy will substantively change our present results.

There is a striking difference in the calculated widths of the two satellites. The second-order approximation of $\hat{\Sigma}$ allows for a qualitative interpretation if we rely upon the spectroscopic assignments given in Ref. 13: While for the higher resonance the ^1S intermediate core state has vanishing exchange contributions, a strong cancellation of direct and exchange diagrams occurs for the lower resonance. It is to be expected that this difference is much reduced if the present approximation of the self-energy is abandoned in favor of a more sophisticated form for $\hat{\Sigma}$.

In conclusion it is clear from these calculations on Be, the simplest system exhibiting an Auger resonance, that the Siegert Green's-function method of I can be used to calculate the energies and widths of both electron scattering and Auger resonances. In future calculations we shall examine the effects of various improved approximations to the self-energy on these results. We shall also employ this method to do calculations on larger atomic and molecular systems where experimental results are available to further assess the method.

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APPENDIX

The following formula for the Slater integral involving Siegert orbitals is applicable provided that $\operatorname{Re}(q+\zeta_3)>0$ with $q\equiv -ik$:

$$
\begin{aligned}
F^{(K)} = {} & \left(\frac{(2\zeta_2)^{2n_2+1}(2\zeta_3)^{2n_3+1}(2\zeta_4)^{2n_4+1}}{(2n_2)!(2n_3)!(2n_4)!}\right)^{1/2} \Bigg[\int_0^\infty dx\, x^{n_3-K} e^{-(q+\zeta_3)x} \int_0^x dy\, y^{n_2+n_4+K-1} e^{-(\zeta_2+\zeta_4)y} \\
& - \int_0^\infty dx\, x^{n_3-K} e^{-(q+\beta+\zeta_3)x} \int_0^x dy\, y^{n_2+n_4+K-1} e^{-(\zeta_2+\zeta_4)y} \\
& + \int_0^\infty dx\, x^{n_2+n_4-K} e^{-(\zeta_2+\zeta_4)x} \left(\int_0^x dy\, y^{n_3+K-1} e^{-(q+\zeta_3)y} - \int_0^x dy\, y^{n_3+K-1} e^{-(q+\beta+\zeta_3)y}\right)\Bigg] \\
= {} & \left(\frac{(2\zeta_2)^{2n_2+1}(2\zeta_3)^{2n_3+1}(2\zeta_4)^{2n_4+1}}{(2n_2)!(2n_3)!(2n_4)!}\right)^{1/2} \Bigg[\sum_{\nu=1}^{n_3-K+1}\left(\frac{(n_3-K)!(n_2+n_4+K+\nu-2)!}{(q+\zeta_3)^{n_3-K-\nu+2}(q+\zeta_2+\zeta_3+\zeta_4)^{n_2+n_4+K+\nu-1}(\nu-1)!}\right. \\
& \left. - \frac{(n_3-K)!(n_2+n_4+K+\nu-2)!}{(q+\beta+\zeta_3)^{n_3-K-\nu+2}(q+\beta+\zeta_2+\zeta_3+\zeta_4)^{n_2+n_4+K+\nu-1}(\nu-1)!}\right) \\
& \times \sum_{\nu=1}^{n_2+n_4-K+1}\left(\frac{(n_2+n_4-K)!(n_3+K+\nu-2)!}{(\zeta_2+\zeta_4)^{n_2+n_4-K-\nu+2}(q+\zeta_2+\zeta_3+\zeta_4)^{n_3+K+\nu-1}(\nu-1)!}\right. \\
& \left. - \frac{(n_2+n_4-K)!(n_3+K+\nu-2)!}{(\zeta_2+\zeta_4)^{n_2+n_4-K-\nu+2}(q+\beta+\zeta_2+\zeta_3+\zeta_4)^{n_3+K+\nu-1}(\nu-1)!}\right)\Bigg].
\end{aligned}
$$

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