Theory of Auger energies in free atoms: Application to the alkaline earths

Donald R. Beck
Physics Department, Michigan Technological University, Houghton, Michigan 49931

C. A. Nicolaides
Theoretical and Physical Chemistry Institutes, National Hellenic Research Foundation,
48 Vasileos Constantinou, Athens 11635, Greece

(Received 9 December 1985)

We calculate, including correlation, relativistic, and radiative effects, the Auger energies associated with the $KL_{3}L_{2,3}(^1P_{1}, ^1D_{2}, ^1S_{0})$ transitions in Mg to be, respectively, 1171.25, 1166.9, 1161.9 eV. The experimental values are, respectively, 1171.0 (1170.85), 1167.1 (1167.0), and 1161.9 (1161.75) eV. For the $KL_{3}L_{2,3}(^1D_{2})$ transition in Ca, we obtain 3275.8 eV and for the $BKL_{1}L_{1}(^1S_{0})$ transition, 96.21 eV, in good agreement with the experimental value of 96.11 eV. Predictions are also made for O and $F\text{ KLL}$ Auger energies.

I. INTRODUCTION

Recent papers in Physical Review A have dealt with the theory and experiment of inner electron binding energies (BE's) and Auger energies (AE's) of free atoms. New experimental values were presented and comparisons were made with theoretical results.

The main theme of these papers was the importance of relativistic and/or correlation effects—something which has been pointed out in the earlier literature as well.

Aksela et al., used experimental values found in the literature or obtained in their laboratory. Extensive comparison was made with multiconfigurational Dirac-Fock calculations, obtained using the computer program of Grant et al. They observed "considerable deviations" (from 1 to 7 eV), which they attributed to "the presence of electron correlation either in the initial or in the final state of the Auger decay." Some of the cases presented by Aksela et al. have been studied by us earlier and recently. A collection of results of binding energies of K- and L-shell electrons is presented in Table I.

Banna and Slaughter analyzed the $2p_{1/2}$ spectrum of atomic potassium and compared the binding energy of the $2p_{1/2}$ and $2p_{3/2}$ levels with previous experiments and the theoretical results of Beck and Nicolaides. These numbers are given in Table I.

Chen et al. presented a series of results based on calculations at the relativistic Dirac-Fock-Slater level with corrections for magnetic-retardation, radiative, and electron correlation effects. The utility of such analyses has been demonstrated by Beck and Nicolaides and Nicolaides et al.

Finally, Bruch et al. presented experimental and theoretical results on the $K$-shell BE's of B and C. Their approach was based on the use of the semiempirical pair energies of Okus and Sinanoglu. The theory and possibility of treating Auug states of open-shell systems in such a way was proposed and implemented by us in the early 1970s. The 1s BE of carbon, which was predicted in Refs. 7 and 15, is included again in Table I.

Given the continuing interest in the accurate prediction of BE's and AE's, as exemplified by the recent Refs. 1–4, we have applied our many-electron theory of such quantities to the calculation of Auger energies in the alkaline-earth metals Be, Mg, and Ca. The predictions agree well with the experimental values for Be and Mg. For Ca, there are no experimental results yet.

II. REVIEW OF THE THEORY OF INNER HOLE STATE AND OF AUGER ENERGIES

Until the early 1970s, the theory of atomic Auger energies was developed and applied in terms of some model based on the independent-particle approximation with or without inclusion of relativistic effects (e.g., see Refs. 20–22 and references therein). The first integrated proposals for the systematic incorporation of many-electron effects, in addition to relativistic and radiative corrections, appeared in Refs. 13–15, 21, 22, 23, 24, 7, and 25.

Fundamental aspects of the Auger phenomenon and related calculations were reviewed recently by Aberg and Howat. In this section, we will bring attention to only certain characteristics of the problems related to the electronic structure of autoionizing states and the corresponding calculation of the Auger energies. For more rigorous discussions and recent developments on the calculation of widths, the reader is referred to Refs. 11, 13, 19, and 26–29.

A. Theory of the nonrelativistic electronic structure of inner hole states

The theory is state specific, i.e., it describes each state of interest with its own optimized zeroth-order wave function and its own, separately optimized, virtual function space. For a recent review of this approach with applications to the electronic structure and properties of excited atoms and molecules, see Ref. 30.

For an autoionizing state, the wave function is separated formally into two components:

$$\psi(E) = a(E)\psi_0 + \int b(E')X_0(E')dE'. \quad (1)$$
TABLE I. Some existing binding \(K\) shell unless otherwise indicated in "Atom" column) and \(KLL\) Auger energies for light atoms (in eV).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Binding energy (eV)</th>
<th>Auger transition</th>
<th>Auger energy (eV)</th>
<th>Experiment or semi-empirical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theory</td>
<td>Experiment</td>
<td>Theory</td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>123.7(^a)</td>
<td>123.6(^b)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>296.3(^c)</td>
<td>296.1(^d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>544.5(^e)</td>
<td></td>
<td>243.6(^f)</td>
<td>243.4(^f)</td>
</tr>
<tr>
<td>F</td>
<td>698.0(^i)</td>
<td></td>
<td>460.5(^i)</td>
<td>460.6(^i)</td>
</tr>
<tr>
<td>Ne</td>
<td>870.3(^j)</td>
<td>870.21(^j)</td>
<td>804.6(^k)</td>
<td>804.46(^k)</td>
</tr>
<tr>
<td>Na</td>
<td>1079.3(^l)</td>
<td>1079.1(^k)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>1311.47(^m)</td>
<td>1311.3(^m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(2p(_{1/2}))</td>
<td>303.7(^n)</td>
<td>303.31(^o)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(2p(_{3/2}))</td>
<td>300.9(^p)</td>
<td>300.56(^q)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>4047.8(^l)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Reference 11.
\(^c\)Reference 15.
\(^d\)Reference 4.
\(^f\)Semiempirical; this work. Like footnote e, except theoretical binding energy was used.
\(^g\)Reference 24.
\(^h\)References 23 and 19.
\(^i\)Reference 17.
\(^j\)Experimental, Ref. 1.
\(^l\)Reference 9.

\(\psi_0\) is bound and \(X'_{EL}(E')\) contains the asymptotic, energy-normalized terms which represent the open channels. Although this separation is naturally dictated by scattering theory and forms the basis for the fundamental analysis of spectroscopic phenomena,\(^{26,31}\) the relevant question here is how to obtain \(\psi_0\) and \(X_{EL}(E')\), and how to analyze them into important or unimportant terms for each observable.

The overwhelming contribution to the total energy comes from \(\psi_0\). Nevertheless, the contribution of the second component to the Auger energy should, in principle, also be calculated, especially since an Auger transition often occurs between two autoionizing states (i.e., the final state could itself be broadened by autoionization). However, for the \(KLL\) Auger transitions studied here, its effect on the transition energy is very small and will not be considered (for example, Nicolaides et al. found\(^{19}\) that for the \(Ne^+\) \(1s^22s^22p^6\) Auger state, the energy shift, \(\Delta\), due to open-channel mixing, is \(-0.1\) eV, while its total energy is \(870.3\) eV above the ground state and the total width is about \(0.25\) eV).

\(\psi_0\) is the square-integrable component describing the initially localized state. Its consistent evaluation for an arbitrary system requires the correct determination of a zeroth-order bound wave function which contains the strongly mixed bound configurations obtained self-consistently. This wave function is composed of the Fermi-sea orbitals which are specific to each state of interest.\(^{17,24,30}\) It is designated as \(\Phi_{FS}\) and is obtained numerically using the program of Froese Fischer\(^{12}\) under the constraints of the correct boundary conditions, number of nodes, satisfaction of the virial theorem, and orthogonality to zeroth-order Hartree-Fock orbitals of lower configurations corresponding to the open channels.\(^{13}\)

The remaining localized components of \(\psi_0\)—which contribute to the stability of the state—are obtained variationally by optimizing the single-, pair-, triple-, etc. symmetry-adapted correlation functions which contain analytic Slater-type virtual orbitals.\(^7\) These correlation functions are constrained to be orthogonal to the same Hartree-Fock orbitals which make up the core of the open channels.\(^{13}\)

Thus, the form of \(\psi_0\) is

\[
\psi_0 = \Phi_{FS} + X_{loc},
\]
where $X_{\text{loc}}$ represents all the localized correlation vectors. In practice, these contain one- and two-symmetry-adapted orbital excitations from $\Phi_{\text{PS}}$. Higher-order excitations have only a small contribution to energy differences of the Auger type.33

The development of the theory of Auger energies along these lines has also contributed to the systematization of useful information as regards approximate cancellation or correlation beyond the state-specific $\Delta$SCF procedure,7,8,11,15 and the introduction of simple electron correlation rules which allow the prior recognition of the important correlation effects in excited states and in various spectroscopies across the Periodic Table.7–10,24,28,34,35

Apart from their calculational value, these rules can be used as a tool for understanding of atomic spectra which do not conform to the independent-particle-model predictions.

We close this section by pointing out two more positive aspects of the state-specific approach. One refers to the use of the well-known $\Delta$SCF approximation the other to the prediction of accurate Auger energies using optical data for the final state.

(a) The state-specific approach also brings out the occasional advantages of the (uncorrelated) well-known term-dependent $\Delta$SCF procedure (which, of course, is state specific). For example, in the case of the $1s$ binding energy of Be (Ref. 11), where the main effect is relaxation, the $\Delta$SCF result (123.34 eV) is in much better agreement with experiment (123.6±0.1 eV) than are two many-electron methods [Green's function (124.5 eV, Ref. 36) and extended Koopmans' (127.9 eV, Ref. 37)] which study the $K$-shell excitation from a correlated ground state.

Calculations at the $\Delta$HF-SCF level (without any approximation for the exchange interaction) can be of much value for the prediction of core binding energies in metals, either through the "excitonic" model7,38,39 or through $ab\initio$ cluster calculations;60 $\Delta$SCF calculations have also been used to evaluate a number of approximations used for the study of chemical shifts.15

(b) In order to avoid excessive computation for Auger energies, the use of optical data for the final state was introduced15 in conjunction with $ab\initio$ state-specific calculations of the initial state. Comparison with experiments using the same optical data, would then test the initial-state binding energy. For C KLL, our early value15 was 243.6 eV, while utilization of a recent experiment's 4 binding energy yields 243.4 eV. For the Ne KLL ($1^1D$) Auger energy, we predicted24 804.6 eV, in agreement with the experimental value18 of 804.557±0.017 eV. Aksela et al.1 quote a theoretical result for this Auger energy of 806.78 eV. As Aberg and Howat have also suggested,26 the combination of theoretical predictions for the initial state with optical data for the final state can prove a useful and economic means for studying inner hole excited states. Table I also contains predictions for O and F KLL Auger energies using this method.

B. Relativistic theory and radiative corrections

Given the absence of a completely relativistic, many-electron theory in Hamiltonian form and the limitations of applying quantum electrodynamics accurately beyond one-electron atoms,44 these effects must be incorporated in the calculation of binding or Auger energies via some approximation.

Our proposal and implementation for the incorporation of radiative effects is presented in Refs. 7 and 23. It is based on the appropriate scaling of the QED results on one-electron ions.42,43

Relativistic effects are computed at the multiconfigurational Dirac-Fock (MCDF) level using the computer program of Desclaux.44 Regarding the analysis given above, this involves the formal replacement of $\Phi_{\text{PS}}$ of Eq. (2) with $\Phi_{\text{RPS}}$. The rigorous incorporation of relativistic correlation using at least the Breit operator is an open subject. An outline of the extension of our theory, now in progress, has been given in Ref. 7(b). Special emphasis on the appropriate choice of electron function spaces was given. As was pointed out in Ref. 35(b), in analogy with the autoionization problem and the orthogonality and boundary conditions imposed there on the one- and many-electron bound functions,13 the use of Dirac-Fock one-positron projection operators on the relativistic correlation functions is expected to alleviate problems of "var- 

ational collapse" into the positron continuum45 with suffi-

cient accuracy. Orthogonality to Dirac-Fock positron or-
bital solutions rather than to some higher-order, correlated po- 

sitron functions is rigorously justified to second order in 

perturbation theory—in analogy with what has been prov- 

en for autoionizing many-electron states.13 Analysis and 

discussions on the need of defining projected relativistic 

operators have been given by Mittleman46 and by Such- 

er.47 For example, Mittleman46 has derived the Dirac- 

Fock projection operators in relation to practical configura-

tion-space Hamiltonians, which were then used to justify current relativistic calculations of the Dirac-

Fock type.

III. METHOD OF APPLICATION AND RESULTS

As is usual in our treatment of binding and Auger ener-
gies, the localized nonrelativistic correlation effects are 

broken into several units which are treated separately. 

This serves three purposes: (1) Some units are essentially 

identical in the initial and final states, and so are not 

 calculated at all. For example, by using the ground state 

of the neutral atom as reference, the $1s^2$ pair energy may 

be taken to be the same for it and the Auger final state. 

(2) A unit is chosen so as to minimize the number of virtual 

radial functions required (here, there are two virtual 

radials per l). This, for example, is characteristic of all 

excitations arising from the same shells. (3) Fragmentation 

into units tends to reduce the number of pair-pair interac-

tions included, which would otherwise have to be balanced 

by including higher-order excitations.

In Table II, we present the various contributions to the 

energy difference between the ground state of Mg and the 

three final states associated with the Auger process, Mg $^{2+}$ 

$1s^22s^22p^63s^2l(3P, 1D, 1S)$. The first row contains the 

nonrelativistic single-configuration numerical Hartree-Fock 

(RHF) results obtained from the program of Froese Fish- 

er.32 Following this, a relativistic calculation is performed
TABLE II. Contributions (in a.u.) to the $KL_{2,3}L_{2,3}$ Auger energy of Mg.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>$E(Mg)$</th>
<th>$\epsilon P_2$</th>
<th>$\epsilon D_2$</th>
<th>$\epsilon S_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHF</td>
<td>-199.614637</td>
<td>-194.561527</td>
<td>-194.394053</td>
<td>-194.144938</td>
</tr>
<tr>
<td>Relativistic</td>
<td>-0.288666</td>
<td>-0.297488</td>
<td>-0.293719</td>
<td>-0.293390</td>
</tr>
<tr>
<td>$\Delta QED$</td>
<td>+0.007</td>
<td>+0.007</td>
<td>+0.007</td>
<td>+0.007</td>
</tr>
<tr>
<td>Internal</td>
<td>-0.021652</td>
<td>-0.042600</td>
<td>-0.042675</td>
<td>-0.042392</td>
</tr>
<tr>
<td>$\epsilon(3s^2)$</td>
<td>-0.012014</td>
<td>-0.002790</td>
<td>-0.002672</td>
<td>-0.002989</td>
</tr>
<tr>
<td>$\epsilon(L, L)$</td>
<td>-0.263426</td>
<td>-0.124152</td>
<td>-0.133041</td>
<td>-0.157342</td>
</tr>
<tr>
<td>$2s^2 \rightarrow 2p^2$</td>
<td>-0.018173</td>
<td>-0.032367</td>
<td>-0.030646</td>
<td>-0.031714</td>
</tr>
<tr>
<td>$\epsilon(L, 3s)$</td>
<td>-0.029328</td>
<td>-0.025114</td>
<td>-0.025437</td>
<td>-0.025333</td>
</tr>
<tr>
<td>Polarization</td>
<td>0.0</td>
<td>-0.054198</td>
<td>-0.055729</td>
<td>-0.00022</td>
</tr>
<tr>
<td>Total</td>
<td>-200.240896</td>
<td>-195.133236</td>
<td>-194.965877</td>
<td>-194.782502</td>
</tr>
</tbody>
</table>

*aSee text for explanations.

With the program of Desclaux,$^{44}$ using a term-dependent electrostatic energy and a finite nucleus model. Two-body relativistic effects (Breit interaction) are evaluated to first order, using the average energy expression. As might be expected, the differential effects among the terms are much smaller than those between Mg and Mg$^{2+}$.

The radiative effects, $\Delta QED$, are referenced to Mg$^+$ as in Ref. 9, and account for the effect of the Lamb shift and vacuum polarization on a single screened 1s electron. Using the work of Huang et al.,$^{48}$ we estimate the differential 2p radiative effects to be below 20 $\mu$eV, and so ignore them.

The first of the nonrelativistic correlation effects, $3s^2 \rightarrow 3p^2$ (labeled "internal" in the table), is seen to be highly dependent on the ionization stage, as was noted elsewhere.$^{9,11}$ For full comparison, the Auger initial state had an internal contribution of $-0.032651$ a.u. The remaining part of the valence-shell $\epsilon(3s^2)$ correlation shows a strong ionization dependence (for Mg$^+$ it is $9-0.008947$ a.u.), but is small enough so the differential effects are modest.

The next entry, $\epsilon(L, L)$, arises from double excitations out of the L shell into either an occupied and virtual radial (2s$^2 \rightarrow 2pV_p$, an example of hole-virtual correlation) or two virtuals. The latter (bivirtual) falls into three categories, classified according to their origin, viz., 2s$^2 \rightarrow 2p$, 2s$^2 \rightarrow 2p^2$, and 2p$^2 \rightarrow 2p$. These bivirtual energies can be expressed as a sum of products of “group factors” and radial pair energies which vary slowly with term, and somewhat less so with stage of ionization, etc. For 2s$^2$, the group factors are the same for Mg, Mg$^{2+}$ (all terms), and for Mg$^+$ ($K$-hole). For 2s$2p$, Mg and Mg$^{2+}$ have the same group factors, whereas for all Mg$^{2+}$ terms are $\frac{5}{2}$ of the former.$^{49}$ To this point, then, $\epsilon(L, L)$ only varies for the different terms of Mg$^{2+}$ due to the variation of "radial pair energies."

For the remaining part, in Mg$^+$ and Mg, the group factors associated with the radial pair energies $\epsilon(2p^21D)$, $\epsilon(2p^21S)$, and $\epsilon(2p^21P)$ are$^{49}$ respectively, 9, 5, and 3. For Mg$^{2+}$, however, these factors are term dependent. For $3P$ they are, respectively, 4, $\frac{5}{2}$, and $\frac{5}{2}$; for $1D$, 3, $\frac{5}{2}$, and $\frac{5}{2}$ and for $1S$, 3, $\frac{5}{2}$, and $\frac{3}{2}$. The value of this is knowing, via calculated results, that $\epsilon(2p^33P) = -0.243$ eV,
TABLE III. Auger energies in the alkaline-earth metals.

<table>
<thead>
<tr>
<th>Species</th>
<th>Final state</th>
<th>Auger energy (eV)</th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{++}$</td>
<td>$KL_2L_2,3(^3P_2)$</td>
<td>1171.4$^b$</td>
<td>1171.08$^d$</td>
<td></td>
</tr>
<tr>
<td>Mg$^{++}$</td>
<td>$KL_2L_2,3(^1D_2)$</td>
<td>1166.9$^b$</td>
<td>1167.0$^d$</td>
<td></td>
</tr>
<tr>
<td>Mg$^{++}$</td>
<td>$KL_2L_2,3(^1S_0)$</td>
<td>1161.9$^b$</td>
<td>1161.75$^d$</td>
<td></td>
</tr>
<tr>
<td>Ca$^{++}$</td>
<td>$KL_2L_2,3(^1D_2)$</td>
<td>3275.8$^b$</td>
<td>96.21$^f$</td>
<td>96.1±0.1$^f$</td>
</tr>
</tbody>
</table>

$^a$1 a.u. = 27.211608 eV.
$^b$This work. The average $^{1}P$ Auger energy is 1171.25 eV (see text for details).
$^c$Reference 51.
$^d$Reference 1.
$^e$See footnote f of Table I.
$^f$See footnote b of Table I.

The energy is 1171.25 eV. It is this value that is compared to experiment. We might observe that nonrelativistically, the 1s hole state in Mg$^{++}$ may undergo an Auger transition to only the $^3D_2$ or $^1S_0$ final state. Transitions to the $^3P_2$ would only be allowed due to relativistic effects. A portion of this is due to the admixture of $^1D_2$ into the $^3P_2$ state (the remaining part would be due to using a relativistic Hamiltonian in the decay matrix element—see Ref. 52). There is a similar admixture of $^1S_0$ into $^3P_0$. Analysis of the relativistic Hartree-Fock result suggests an admixture of 0.03 for the $^1D_2$ component. Thus one predicts the $^3P_2$ intensity to be $\sim1000$ of the $^1D_2$ from this cause which is in agreement with earlier theoretical work.33–35 Experimentally, the ratio is more like 1/33; clearly, a more thorough theoretical investigation would be desirable.

In Table IV, the various contributions to the energy difference between the ground state of Ca and the Ca$^{++}$ 1s$^2$2s$^2$2p$^4$3s$^2$3p$^6$4s$^2$ $^1D$ Auger final state are given. Most entries were obtained in the same manner as they were for Mg/Mg$^{++}$.

For $\Delta$QED, however, we did reexamine the role of radiative corrections to the 2p levels by using the results of Huang et al.,48 and accounting for the varying occupancies of 2p$_{1/2}$ and 2p$_{3/2}$ in the relativistic configurations used to construct the $^1D$ final state. While individual terms were significant, the net effect (Ca versus Ca$^{++}$) was less than 5 μeV, and so can be ignored.

The calculation of $\epsilon(M,4s)$, which includes 4s polarizations in Ca$^{++}$, presented a somewhat novel feature. Due to the higher ionicity in Ca$^{++}$, the 3d drops below the 4s (4s remains below 3d in Ca and Ca$^{++}$ for the configurations of interest), which resulted in four configurations, viz., $2p^6(^3P)4s^3(^3D)$, $2p^6(^1D)3d^2(^1S)$, $2p^6(^1D)3d^34s(^1D)$, and $2p^6(^1D)3d^34d(^1S)$, being below $2p^6(^1D)4s$ $^1S$. There are actually quite a few others, but these do not directly connect to our RHF vector, and are thus ignored.

So we have the situation of a perturber (namely the RHF) embedded in several Rydberg series. As has been noted in the past,56 it is difficult to find a common orthonormal set of radial functions that properly describes both off-diagonal and diagonal matrix elements. Here we have chosen to adopt an ad hoc procedure like the one used earlier56—we use all the radial of the RHF function, a 3d from ‘‘3d $^2$,” and a 4d from ‘‘3d 4d,” which is then orthogonalized to the 3d. Separate RHF runs on the lower four configurations are performed to establish the amount of energy to be added to each of the diagonal matrix elements computed from the common orthonormal set of configurations below the RHF solution (the so-called56 Down Shift Model or DSM). A few additional Rydberg functions, representing nearby higher configurations, were then added and shifted, and finally virtuals, which were iterated.

One may inquire whether there is a significant probability that a more energetic Auger electron would be emitted, with a concomitant energetically lower final state, e.g., how probable is $2p^6(^1D)3d^2(^1S)$? Since none of the squares of the coefficients of the four lower configurations exceeds 0.01, we regard it as fairly unlikely.

The large relative size of $\epsilon(M,4s)$ correlation is also in part due to the greater importance of the 3d, but here the RHF result is the lowest state of interest, so no special techniques need be applied. Finally, as remarked earlier,9 future work might include examining the extent of non-transferability of the purely M-shell correlation.

Our prediction for the $KL_2L_2,3(^1D_2)$ Auger energy for Ca is obtained using the theoretical binding energy of Ref. 9, and is given in Table III. The $KL_1L_1(^1S_0)$ Auger energy of Be is also shown in the table, and was obtained using the theoretical binding energy11 and optical measurement.

It can be seen that where experimental values exist, theory and experiment are in excellent (≤0.2-eV difference) agreement, and that even theoretical values of ten years ago have stood the test of time rather well.

**ACKNOWLEDGMENTS**

One of us (D.R.B.) wishes to thank the National Science Foundation for partial support of this work (under Grants No. PRM-81-11589 and No. PHY-85-06177).
33. We point out that for certain excited states, the existence of an inner hole causes higher-order correlations to be relatively more important (e.g., see Ref. 30 for the effect of triple excitations in Cl KL 3s 3p 5S).
35. C. A. Nicolaides and D. R. Beck, in Excited States in Quantum Chemistry, Ref. 7, p. 143; (b) see p. 178 of this reference.