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

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We calculate, including correlation, relativistic, and radiative effects, the Auger energies associated with the $KL_{2,3}L_{2,3}(^3P, ^1D_2, ^1S_0)$ 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 $KL_{2,3}L_{2,3}(^1D_2)$ transition in Ca, we obtain 3275.8 eV and for the Be $KL_1L_1(^1S_0)$ transition, 96.21 eV, in good agreement with the experimental value of 96.11 eV. Predictions are also made for O and F *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.[1–4] 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.*[1] 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.*[5,6] 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.*[1] have been studied by us earlier[7,8] and recently.[9] A collection of results of binding energies of *K*- and *L*-shell electrons is presented in Table I.

Banna and Slaughter[2] analyzed the $2p$-core 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.[7,8] These numbers are given in Table I.

Chen *et al.*[3] 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[7,10] and Nicolaides *et al.*[11]

Finally, Bruch *et al.*[4] 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 Oksuz and Sinanoglu.[12] The theory and possibility of treating Auger states of open-shell systems in such a way was proposed and implemented by us in the early 1970s.[13–15] 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[7–11,13–15] 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, 23, 24, 7, and 25.

Fundamental aspects of the Auger phenomenon and related calculations were reviewed recently by Aberg and Howat.[26] 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.[7–10,13–15] 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:

$$\psi(E) = a(E)\psi_0 + \int b^E(E')X^E_{\mathrm{as}}(E')dE' . \quad (1)$$

TABLE I. Some existing binding (*K* shell unless otherwise indicated in "Atom" column) and *KLL* Auger energies for light atoms (in eV).

| | | | | Auger energy (eV) | |
|---|---|---|---|---|---|
| | Binding energy (eV) | | | | Experiment or semi- |
| Atom | Theory | Experiment | Auger transition | Auger Theory | empirical |
| Be | 123.7[a] | 123.6[b] | | See Table III | |
| C | 296.3[c] | 296.1[d] | $KL_1L_1(^3P)$ | 243.6[c] | 243.4[e] |
| O | 544.5[c] | | $KL_1L_1(^3P)$ | 460.5[c] | 460.6[f] |
| F | 698.0[g] | | $KL_{2,3}L_{2,3}(^2D)$ | | 641.4[f] |
| Ne | 870.3[h] | 870.21[i] | $KL_{2,3}L_{2,3}(^1D)$ | 804.6[h] | 804.46[j] |
| | | 870.3[p] | | 806.9[q] | |
| Na | 1079.3[g] | 1079.1[k] | | | |
| Mg | 1311.47[l] | 1311.3[m] | | See Table III | |
| K($2p_{1/2}$) | 303.7[n] | 303.31[o] | | | |
| K($2p_{3/2}$) | 300.9[n] | 300.56[o] | | | |
| Ca | 4047.8[l] | | | See Table III | |

[a] Reference 11.

[b] P. Bisgaard, R. Bruch, P. Dahl, B. Fastrup, and M. Robro, Phys. Scr. **17**, 49 (1978).

[c] Reference 15.

[d] Reference 4.

[e] Experimental, this work, using experimental [C. E. Moore, *Atomic Energy Levels* (U.S. GPO, Washington, D.C., 1949), Vol. 1] optical energy.

[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.

[k] M. S. Banna, B. Wallbank, D. C. Frost, C. A. McDowell, and J. S. H. Q. Perera, J. Chem. Phys. **68**, 5459 (1978).

[l] Reference 9.

[m] H. Agren, J. Nordgren, L. Selander, C. Nordling, and K. Siegbahn, J. Electron Spectros. Relat. Phenom. **14**, 27 (1978); W. Mehlhorn, B. Breuckmann, and D. Hausamann, Phys. Scr. **16**, 177 (1979). See also Ref. 16.

[n] Reference 8.

[o] Reference 2.

[p] Reference 18.

[q] Ch. Briancon and J. P. Desclaux, Phys. Rev. A **13**, 2157 (1976).

$\psi_0$ is bound and $X_{as}^{E}(E')$ 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 $X_{as}(E)$, 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 $Ne^+$ $1s2s^22p^6$ 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.[7,24,30] It is designated as $\Phi_{FS}$ and is obtained numerically using the program of Froese Fischer[32] 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

$$\psi_0=\Phi_{FS}+X_{loc}\ , \tag{2}$$

where $X_{\text{loc}}$ represents all the localized correlation vectors. In practice, these contain one- and two-symmetry-adapted orbital excitations from $\Phi_{\text{FS}}$.[7] 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 ΔSCF 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 the 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 ΔSCF 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 ΔSCF 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 ΔSCF 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's (127.9 eV, Ref. 37)] which study the $K$-shell excitation from a correlated ground state.

Calculations at the ΔHF-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" model[7,38,39] or through *ab initio* cluster calculations;[40] ΔSCF 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 introduced[15] 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 value[15] was 243.6 eV, while utilization of a recent experiment's[4] binding energy yields 243.4 eV. For the Ne $KLL\,(^1D)$ Auger energy, we predicted[24] 804.6 eV, in agreement with the experimental value[18] 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,[41] 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 $\Phi_{\text{FS}}$ of Eq. (2) with $\Phi_{\text{RFS}}$. 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 "variational collapse" into the positron continuum[45] with sufficient accuracy. Orthogonality to Dirac-Fock positron orbitals rather than to some higher-order, correlated positron functions is rigorously justified to second order in perturbation theory—in analogy with what has been proven for autoionizing many-electron states.[13] Analysis and discussions on the need of defining projected relativistic operators have been given by Mittleman[46] and by Sucher.[47] For example, Mittleman[46] has derived the Dirac-Fock projection operators in relation to practical configuration-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 energies, 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 interactions 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, $\text{Mg}^{2+}$ $1s^22s^22p^43s^2(^3P,^1D,^1S)$. The first row contains the nonrelativistic single-configuration numerical Hartree-Fock (RHF) results obtained from the program of Froese Fischer.[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.

| | | | $E(\mathrm{Mg}^{2+})$ | |
|---|---|---|---|---|
| Quantity[a] | $E(\mathrm{Mg})$[b] | $^3P_2$ | $^1D_2$ | $^1S_0$ |
| RHF | −199.614 637 | −194.561 527 | −194.394 053 | −194.144 938 |
| Relativistic | −0.288 666 | −0.297 488 | −0.293 719 | −0.293 390 |
| ΔQED | +0.007 | +0.007 | +0.007 | +0.007 |
| Internal | −0.021 652 | −0.042 600 | −0.042 675 | −0.042 392 |
| $\varepsilon(3s^2)$ | −0.012 014 | −0.002 790 | −0.002 672 | −0.002 989 |
| $\varepsilon(L,L)$ | −0.263 426 | −0.124 152 | −0.133 041 | −0.157 342 |
| $2s^2 \rightarrow 2p^2$ | | | | −0.084 384 |
| $\varepsilon(L,3s)$ | −0.018 173 | −0.032 367 | −0.030 546 4 | −0.031 714 |
| $\varepsilon(1s,L)$ | −0.029 328 | −0.025 114 | −0.025 437 | −0.025 133 |
| Polarization | 0.0 | −0.054 198 | −0.055 729 | −0.007 22 |
| Total | −200.240 896 | −195.133 236 | −194.965 877 | −194.782 502 |

[a] See text for explanations.
[b] From Ref. 9.

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 $\mathrm{Mg}^{2+}$.

The radiative effects, ΔQED, are referenced to $\mathrm{Mg}^+$ 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 $\mu$H, 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[9] an internal contribution of −0.032 651 a.u. The remaining part of the all-valence-shell $\varepsilon(3s^2)$ correlation shows a strong ionization dependence (for $\mathrm{Mg}^+$ it is[9] −0.008 947 a.u.), but is small enough so the differential effects are modest.

The next entry, $\varepsilon(L,L)$, arises from double excitations out of the $L$ shell into either an occupied and virtual radial ($2s^2 \rightarrow 2pV_p$, an example[7] of hole-virtual correlation) or two virtuals. The latter (bivirtual) falls into three categories, classified according to their origin, viz., $2s^2 \rightarrow$, $2s2p \rightarrow$, and $2p^2 \rightarrow$. These bivirtual energies can be expressed[49] 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[49] for Mg, $\mathrm{Mg}^{2+}$ (all terms), and for $\mathrm{Mg}^+$ ($K$-hole). For $2s2p$, Mg and $\mathrm{Mg}^+$ have the same group factors, whereas those for all $\mathrm{Mg}^{2+}$ terms are $\frac{2}{3}$ of the former.[49] To this point, then, $\varepsilon(L,L)$ only varies for the different terms of $\mathrm{Mg}^{2+}$ due to the variation of "radial pair energies."

For the remaining part, in $\mathrm{Mg}^+$ and Mg, the group factors associated with the radial pair energies $\varepsilon(2p^2\,{}^3P)$, $\varepsilon(2p^2\,{}^1D)$, and $\varepsilon(2p^2\,{}^1S)$ are,[49] respectively, 9, 5, and 1. For $\mathrm{Mg}^{2+}$, however, these factors are term dependent. For $^3P$ they are, respectively, 4, $\frac{5}{3}$, and $\frac{1}{3}$; for $^1D$, 3, $\frac{8}{3}$, and $\frac{1}{3}$ and for $^1S$, 3, $\frac{5}{3}$, and $\frac{4}{3}$. The value of this is knowing, via calculated results, that $\bar{\varepsilon}(2p^2\,{}^3P) = -0.243$ eV, $\bar{\varepsilon}(2p^2\,{}^1D) = -0.397$ eV and $\bar{\varepsilon}(2p^2\,{}^1S) = -1.17$ eV, quantities which are, to a large extent, independent of term. To summarize, the variation among $\varepsilon(L,L)$ for the various terms is fundamentally due to the change in the group factors associated with $2p^2 \rightarrow$. The radial pair energies are *not* sufficiently invariant to degree of ionization to ascribe the principal variation in $\varepsilon(L,L)$ there to the group factors, however. Both the variation in $\varepsilon(L,L)$, and the internal correlation $2s^2 \rightarrow 2p^2$ which exists only for $^1S$ of $\mathrm{Mg}^{2+}$ (shown in the next row) are differentially quite important contributors to the Auger energy.

For $\varepsilon(L,3s)$ and $\varepsilon(1s,L)$ there is no difference[49] in the group factors for the various terms of $\mathrm{Mg}^{2+}$. Hence, any change is due to the radial factors, and, as can be seen from the table, this is small. On the other hand, for Mg, these contributions should be $\frac{3}{2}$ times larger on the basis of the group factors. As this is not so, we can see intershell radial factors can depend strongly on ionization as has been observed elsewhere.[9]

The remaining contributions arise from the polarizations (single excitation to virtual subshells). By far, the largest contributions arise from $2s \rightarrow V_d$ and, to a lesser extent, from $2p \rightarrow V_f$, as can be observed from the table, where these are absent in the $^1S$ term.

The remaining excitations are those which violate Brillouin's theorem. For $\mathrm{Mg}^+$, these were found to be much larger[9] ($\sim -0.022$ a.u. total). What accounts for this difference? For both $\mathrm{Mg}^+$ and $\mathrm{Mg}^{2+}$ $^3P$, the $2s \rightarrow V_s$ is the largest. In the former, the off-diagonal matrix element is $-\frac{3}{2}R^0\,(1s2s;\ V_s\ 1s) = -0.3429$ a.u. and in the latter, $\frac{2}{3}\ R^1(2s2p;\ 2p\ V_s) = 0.1038$ a.u., and it is this factor which accounts for the relative decline of the effect in $\mathrm{Mg}^{2+}$.

Using the total energy for $\mathrm{Mg}^+$ given in Ref. 9, we establish our results for the $KL_{2,3}L_{2,3}$ Auger energies which we present in Table III, together with the experimental values of Aksela *et al.*[1] As can be seen from the table, our results are in excellent agreement with the available experimental values.[1,50] Using the low-$Z$ Pauli approximation,[51] and the RHF wave function, the fine-structure splitting for the $^3P$ terms is $^3P_0$-$^3P_1 = 0.0999$ eV, and $^3P_1$-$^3P_2 = 0.215$ eV. The $^3P$ weighted average energy is then 0.153 eV above the $^3P_2$ level, so that the weighted Auger

TABLE III. Auger energies in the alkaline-earth metals.

| Species | Final state | Auger energy (eV)[a] Theory | Experiment |
|---|---|---|---|
| Mg$^{2+}$ | $KL_{2,3}L_{2,3}(^3P_2)$ | 1171.4[b] | 1171.0[c]<br>1170.85[d] |
| Mg$^{2+}$ | $KL_{2,3}L_{2,3}(^1D_2)$ | 1166.9[b] | 1167.0[d]<br>1167.1[c] |
| Mg$^{2+}$ | $KL_{2,3}L_{2,3}(^1S_0)$ | 1161.9[b] | 1161.75[d]<br>1161.9[c] |
| Ca$^{2+}$ | $KL_{2,3}L_{2,3}(^1D_2)$ | 3275.8[b] | |
| Be$^{2+}$ | $K_1L_1(^1S_0)$ | 96.21[e] | 96.1±0.1[f] |

[a] 1 a.u. = 27.211 608 eV.

[b] This work. The average "$^3P$" 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.

TABLE IV. Contributions (in a.u.) to the $KL_{2,3}L_{2,3}(^1D_2)$ Auger energy of Ca.

| Quantity[a] | $E$(Ca)[b] | $E$(Ca$^{2+}$ $^1D_2$)[c] |
|---|---|---|
| RHF | −676.758 186 | −648.407 936 |
| Relativistic | −2.761 420 | −2.748 203 |
| ΔQED | +0.050 68 | +0.050 68 |
| Internal | −0.019 415 | −0.034 571 9 |
| $\varepsilon(4s^2)$ | −0.009 052 | −0.001 552 |
| $\varepsilon(L,L)$ | −0.246 463[c] | −0.113 782 |
| $\varepsilon(L,M)$ | −0.075 186 3[c] | −0.074 204 2 |
| $\varepsilon(K,L)$ | −0.029 451 | −0.030 345 |
| $\varepsilon(M,4s)$ | −0.026 466 | −0.058 506 6 |
| Polarization | 0.0 | −0.087 789 |
| Total | −679.874 959 | −651.506 21 |

[a] See text for explanation.

[b] From Ref. 9, unless otherwise indicated.

[c] This work.

energy is 1171.25 eV. It is this value that is compared to experiment. We might observe that nonrelativistically, the 1$s$ hole state in Mg$^+$ may undergo an Auger transition to only the $^1D_2$ 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 $\sim\frac{1}{1000}$ of the $^1D_2$ from this cause which is in agreement with earlier theoretical work.[53–55] 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$^{2+}$ $1s^22s^22p^43s^23p^64s^2$ $^1D$ Auger final state are given. Most entries were obtained in the same manner as they were for Mg/Mg$^{2+}$.

For ΔQED, however, we did reexamine the role of radiative corrections to the 2$p$ 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[44] the $^1D$ final state. While individual terms were significant, the net effect (Ca versus Ca$^{2+}$) was less than 5 $\mu$H, and so can be ignored.

The calculation of $\varepsilon(4s^2)$, which includes 4$s$ polarizations in Ca$^{++}$, presented a somewhat novel feature. Due to the higher ionicity in Ca$^{++}$, the 3$d$ drops below the 4$s$ (4$s$ remains below 3$d$ in Ca and Ca$^+$ for the configurations of interest), which resulted in four configurations, viz., $2p^4(^3P)4s\,3d\,(^3D)$, $2p^4(^1D)3d^2(^1S)$, $2p^4(^1D)3d\,4s\,(^1D)$, and $2p^4(^1D)3d\,4d\,(^1S)$, being below $2p^4(^1D)4s^2(^1S)$. 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 earlier[56]—we use all the radials of the RHF function, a 3$d$ from "$3d^2$," and a 4$d$ from "3$d$ 4$d$," which is then orthogonalized to the 3$d$. 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-called[56] 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 $2p^4(^1D)3d^2(^1S)$? 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 $\varepsilon(M,4s)$ correlation is also in part due to the greater importance of the 3$d$, 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 nontransferability of the purely $M$-shell correlation.

Our prediction for the $KL_{2,3}L_{2,3}(^1D_2)$ 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 energy[11] and optical measurement.

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

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