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Relativistic and many-body effects in first-row transition-metal negative ions: Three Zn^- bound states

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In this work relativistic and many-body effects in transition-metal ions are treated independently. For the former, we have written an automated program which provides level-dependent (J) structure input (for both the electrostatic and the magnetic portion of the Breit operator) to Desclaux's multiconfigurational Dirac-Fock program. Also, the nonrelativistic treatment of many-body effects for these atoms via the configuration-interaction (CI) technique has been made much more efficient, in part by the removal of unnecessary (through first-order) parents, so as to make computational costs competitive with those associated with smaller species. We predict that all levels of Zn^- $3d^9 4s4p^3\,{}^6D_J$ are bound, with the lowest $J=\frac{9}{2}$ bound by 0.810 eV and the highest $J=\frac{1}{2}$ by 0.511 eV, that Zn^- $3d^{10}4s4p^2\,{}^4P_J$ is bound by 0.169 eV ($J=\frac{1}{2}$) and 0.136 eV ($J=\frac{5}{2}$), and that Zn^- $3d^{10}4p^3\,{}^4S_{3/2}$ is bound by 0.566 eV. The complete fine structure is given as well as the electric dipole oscillator strength for the ${}^4P \rightarrow {}^4S^\circ$ transition. All states are found to consist of at least 90% pure LS coupling. Finally, the configuration-interaction program referred to above will soon be modified to do relativistic CI calculations, thus removing the separability assumption.

I. INTRODUCTION

In the first-row transition metals, situations where both relativity and many-body effects are important occur frequently enough so as to be routine. Certainly consideration of the effects of relativity is essential[1] when a $3d$ electron is "converted" to $4s$ or vice versa. Correlation effects are well known by now to be pervasive throughout the Periodic Table and are always important when it comes to electron affinities. But certain novel features are added[2–7] when first-row transition-metal atoms are considered, relating to the large and varied basis sets needed (one- and N-electron), the role of the "core," and the enhanced role of higher-order (triple and quadruple) excitations.

In this work we focus on negative-ion states of Zn obtained by adding a $4p$ electron to the nonrelativistic threshold. Because the additional electron is diffuse ($\langle r \rangle_{4p} \approx 3.7$–$5.2$ a.u.) relativistic effects on the electron affinity (EA) are modest. This is fortunate, because as yet there is no combined relativistic-correlation theory capable of treating a basis of up to several thousand N-electron functions, although that is one of the eventual aims of our project. The relative isolation of the $4p$ subshell coupled with the terms investigated also serves to depress the usual[7] importance of higher-order excitations.

For two of the states, Zn^- ${}^4P$ and ${}^6D$, relativity is the dominant mechanism contributing to the decay of the state (the third state Zn^- ${}^4S^\circ$ also decays by the nonrelativistic electric dipole process). If the lifetime of the state is long enough, say ≥ 1 ns, then the state may be regarded as bound in the usual sense. On the other hand, lifetimes on the order of 10^{-14} s are characteristic of resonances. Calculations of such lifetimes involve[8] the subtle interplay of relativistic effects (on wave functions and the decay Hamiltonian) with those of electron correlation; moreover, they can be highly J dependent. Relativistic effects on lifetimes will not be treated in this work; states will be considered bound when they fall below the threshold of the same symmetry (S, L, and J).

In Sec. II we briefly outline existing many-body theory in use and present the details of the recent improvements. In Sec. III we present and analyze the results obtained from the methods of Sec. II. In Sec. IV the relativistic formalism is summarized, with a particular focus on the angular momentum algebraic results. In Sec. V the relativistic contributions to the electron affinities are obtained and discussed.

II. NONRELATIVISTIC MANY-BODY THEORY

We treat many-body effects within a perturbation-directed variational configuration-interaction (CI) framework.[9,10] The zeroth-order function here is the restricted Hartree-Fock solution Φ obtained from the Froese-Fisher program.[11] A first-order correlated wave function is constructed by making single and double subshell excitations into all-open or partly open subshells, consistent with the contribution surviving in first order. Obviously, this means the correlating configuration must have the same total S, L, and parity that Φ does. In the case of double excitations such as $n_il_in_jl_j \rightarrow v_{1a}v'_{1b}$ it also means that the ranges $[\,|l_i-l_j|, l_i+l_j\,]$ and $[\,|l_a-l_b|, l_a+l_b\,]$ must overlap. Here, v indicates the one-electron virtual space. Any portion of the second-order function (triple and quadruple excitations) thought to contribute differentially significantly (i.e., directly to the EA) would also be added.

Construction of the correlation configurations obviously postdates knowledge of the existence of a one-electron virtual space (VS). Formally, in first order the azimuthal symmetries of these functions can be cut off[10] at $3l_{\max}$, where $l_{\max}$ is the maximum l appearing in Φ; for excitations into two VS's, the rule is based on computational experience rather than perturbation theory. In the first-row transition metals, $l \leq 6$. In our approach[9,10] the radial parts of the VS's are represented as a linear combination of Slater-type orbitals (STO's), with exponents selected by the CI process. Generally, it is found that excitations arising from the same subshell(s) can share a common set of STO's; but how many are needed per l per set?

In the past, two have been found to give about 85% of the correlation energy. Recent evidence suggests, however, that $3d^2$ pairs[12–16] and $3p3d$ pairs[7] require a third, diffuse, d and f VS to reach this level of accuracy.

Previously[9,10] we constructed the N-electron symmetry-adapted functions (SAF's) from Slater determinants following the method of Schaeffer and Harris[17] by diagonalizing a linear combination of $\hat{S}^2$ and $\hat{L}^2$ matrices. The presence of open d subshells often has the consequence that a *single* correlation configuration can have 100 SAF's associated with it, as well as ~ 1500 Slater determinants. Problems of this size, however, cannot be conveniently handled by diagonalization due to the large matrix setup costs and the lack of a dependable multiroot (~ 100) diagonalizer.

Recently[18] we revived the Bartlett-Condon-Beck method (BCB), originally due to Bartlett,[19] which breaks the configuration into two parts so that each part can be treated conventionally[18] (e.g., Ref. 17 combined with step-up and step-down operators to maintain phase) and then reassembled at essentially no cost.[18] For "large" cases (100–200 determinants, a few SAF's) where the two methods could be compared, the BCB method was two orders of magnitude faster. For the transition metals, we have found it necessary, at times, to break the initial configuration into three parts[18] in order to reduce the complexities of each part, and simultaneously restrict[10] the subcouplings to those which interact with the zeroth-order (e.g., Hartree-Fock) vector (otherwise we would have ~ 100 SAF's).

This removes only part of the bottleneck, however. To illustrate, in lighter species one may have ~ 50–75 configurations with 2–3 SAF's, on average (and on average fewer than 100 determinants). In transition-metal ions those 50–75 configurations may have 50 SAF's (400–500 determinants on average), leading to an energy matrix of size 2500–3750. If we could find some way to reduce greatly the number of SAF's we would no longer have a computational bottleneck.

Frequently, a first-order wave function is sufficient; the primary characteristic of such a wave function is that the correlated SAF must have a nonzero matrix element with the zeroth-order function. But, as has been noted by Bunge[20] for energies, and us for oscillator strengths,[21] the minimum number of SAF's (i.e., the smallest number of survivors, under all possible orthonormal mappings) may be very much less than the total. For energy, this minimum is equal to the number of independent radial integrals appearing in the first-order matrix element [N.B. in the case of single subshell excitations which preserve symmetry, there is only one composite integral (see, e.g., Ref. 22) representing core-valence and one-body effects; if there is a symmetry change, there are no core-valence or one-body integrals]. To illustrate, suppose the zeroth-order function is $3d^9 4s4p\,^3\,{}^6D^\circ$, and the excitation $3d^2 \rightarrow 4pv_f$ is of interest. There are 63 surviving SAF's but only two independent radial integrals: $R^1(3d3d;4pV_f)$ and $R^3(3d3d;4pV_f)$. Thus one could reduce the SAF's from 63 to 2, and in fact, this has now been fully automated in an algorithm we call REDUCE. In the problems discussed here, this reduces the energy matrix from over 1000 SAF's (not very manageable) to under 100. Obviously, all or part of the first-order function may serve as a reference function if necessary, but the gains would not be as striking then.

The above reduction eliminates all higher-order SAF's, which is entirely consistent with much of our earlier work,[9,10] where we used subparentalization to remove SAF's not interacting with the zeroth-order vector. Here the validity was checked for Zn^- by running the all-SAF case for $3d^2 \rightarrow V_d^2 + V_f^2$ and comparing it to the reduced result. For these configurations, which dominate the correlation function, the loss in energy is only 0.029 millihartree (entirely tolerable in the present context). We note however that significant contributions, at least in terms of coefficients, from higher-order SAF's are not totally unknown, as Bunge's work[23] on Li^- and ours[24] on Be^- illustrates.

Higher-order effects associated with configurations related to the Hartree-Fock one through triple and quadruple excitations were not investigated here. In Cu $3d^{10}4s$ and Cu^- $3d^{10}4s^2$ the only higher-order effects of this type found to be differentially important to date[7] were $3d^2 4s^2$ excitations in Cu^-, with contributions near 0.2 eV. In Zn^- such effects should be more strongly suppressed due to the reduction in differential valence-shell correlation.

In larger problems, over 90% of the computational time is spent setting up the energy matrix element structure (each matrix element is represented as a linear combination of radial integrals). For each determinant, the bulk of the spin orbitals are packed into the bits of a single word, with the remainder (VS's) stored in individual byte-sized words. In a comparison of determinants, which begins with the outermost spin orbitals, the bit portions involve only a linear process. This approach seems to offer a good compromise between determinant storage needs and comparison speeds. Presently, about the same amount of time is required to evaluate the survivors (typically 3–5 % of the total for large problems) as to compare all determinants whose configurations interact (with a configurational pretest imposed). The major future improvement in this area will be to generate a "configurational" structure table (or "Rydberg series table") as in Ref. 22, which would allow use of any appropriate existing energy matrix element structure. To illustrate simply: If there were three two-electron configurations $1s^2, 2s^2, 3s^2, {}^1S$, one need explicitly develop only two out of six energy matrix element structures, e.g., $\langle 1s^2 | H | 1s^2 \rangle$ and $\langle 1s^2 | H | 2s^2 \rangle$. All other structures,

TABLE I. Energy contributions to electron affinity (EA) of Zn^- $3d^9 4s4p^3\ {}^6D^\circ$.

Energy contribution type[a]	${}^6D^\circ$	Threshold $3d^9 4s4p^2\ {}^5D$	Contribution to EA (eV)
RHF	−1777.423 94	−1777.403 70	+0.551
N-shell correlation	−26.62	−16.08	+0.287
$\varepsilon(3d,4p)$	−23.01	−21.58	+0.039
$\varepsilon(3d,4s)$	−15.68	−19.26	−0.097
$\varepsilon(3p,4p)$	−2.93	−2.46	+0.013
$\varepsilon(3d,3d)$[b]	−319.80	−318.71	+0.0297
Nonrelativistic (total)			+0.818
Relativistic ($J=9/2$)			+0.810

[a] RHF energy units are hartrees. The remainder are millihartree.

[b] Includes single excitations from $3d$ −0.005 915 a.u. from Zn^- and −0.005 7395 a.u. from Zn.

e.g., $\langle 1s^2 | H | 3s^2 \rangle$, could be obtained from these 2 through a change of principal quantum number (the existence of more than one SAF per configuration just complicates the programming).

III. NONRELATIVISTIC RESULTS

During our survey of energetically low-lying potentially bound states of transition-metal negative ions carried out at the restricted Hartree-Fock (RHF) level,[11] three possible bound state candidates were uncovered in Zn^-: $3d^{10}4s4p^2\ {}^4P$, $3d^{10}4p^3\ {}^4S^\circ$, and $3d^9 4s4p^3\ {}^6D^\circ$. [Electron affinities obtained using the RHF approximation were 0.018, 0.149, and 0.551 eV, respectively (see Tables I and II)]. These are analogous to states we studied[24,25] in Mg^- and Be^-, the first of which was also examined by Bunge *et al.*[26]

The N-shell correlation was obtained from a radial basis of two optimized Slater-type orbitals for each l ($l \leq 5$). The form of the correlation was that allowed by first-order perturbation theory (single and double subshell excitations from the RHF configurations). As shown in Tables I and II, the differential contribution to the electron affinity ranges from +0.2 to +0.3 eV; contributions from $l > 3$ were minimal.

Excitations from the $3d$, $4p$, and $3d,4s$ subshells in the presence of N-shell correlation were then included, with the existing radial set augmented with a third set of optimized STO's ($l \leq 4$). Since many configurations gave rise to a large number of parents (e.g., $3d4p \rightarrow v_l v_{l+1}$ in ${}^5D$ has 63 parents for $l \geq 1$), the REDUCE algorithm was employed. The net differential correlation from these is only +0.039 eV. The ${}^5D$ wave function had, at this stage, 194 SAF's and took about 5.5 CPU h on a VAX 11/750 to construct; the ${}^6D^\circ$ had 157 SAF's and took 3.5 h of CPU time.

We have chosen to explore the role of the core by examining the contribution of pair excitation from the $3d$ subshell for ${}^6D^\circ$ and its threshold, ${}^5D$. A separate run ($\text{RHF} + 3d^2 \rightarrow$) was done using a 2STO-$l$ basis ($l \leq 4$) with a diffuse d and f added. Using the REDUCE algorithm we find (Table I) a contribution of about 8.70 eV to each state, with the contribution to the EA being (Table I) only about +0.03 eV. For Cu^- and Cu we find[7] that the $3d^2$ contribution to the EA is about +0.5 eV, with the contribution to each state being close to $\frac{5}{4}$ of that

TABLE II. Energy contributions to the electron affinities (EA) of Zn^- $4p^3\ {}^4S_{3/2}$ and Zn^- $4s4p^2\ {}^4P_J$.

Energy contribution type[a]	$4p^3\ {}^4S^\circ_{3/2}$	Threshold $4p^2\ {}^3P_0$	Contribution to EA (eV)
RHF	−1777.554 248	−1777.548 770	+0.149
N-shell correlation	−19.17	−7.17	+0.328
$\varepsilon(3d,4p)$	−29.11	−24.16	+0.135
Relativity			−0.046
Total			0.566
	$4s4p^2\ {}^4P_J$	$4s4p\ {}^3P_0$	
RHF	−1777.751 66	−1777.751 000	+0.018
N-shell correlation	−14.15	−5.83	+0.226
$\varepsilon(3d,4s+4p)$	−33.97	−35.11	−0.031
Total, nonrelativistic			+0.213
Other[b]			+0.150
Total, with relativity ($J=1/2$)			+0.169

[a] The nonrelativistic restricted Hartree-Fock energy is in hartrees; the remaining contributions are in millihartree.

[b] Reference 26.

from Zn^- and Zn, which would be predicted[10] by group theory, if radial transferability was exact, and second- and higher-order effects could be neglected. In Cu and Cu^- we also found[7] the $3p3d$ pairs to contribute about $+0.05$ eV to the EA.

These findings demonstrate that $3d^2$ excitations make marginal contributions to the Zn^- EA and suggest that deeper core contributions may be ignored for Zn^- ^6D and Zn ^5D. The difference between Cu^- and Cu and Zn^- and Zn is likely ascribable to the relative isolation of the $4p$ subshell in Zn^-,Zn, compared to the $4s$ subshell in Cu^- and Cu.

In Cu^- and Cu, essentially all the triple and quadruple excitations found[7] to be important contributors to the EA were of the type $3d^2 4s^2 \rightarrow 4p^2 xy$ and $3d4s^2 \rightarrow 4p^2 z$, where x, y, and z were VS's. Obviously, these are present in Cu^- and not in Cu; they also involve a strong "internal" correlation. In Zn^- there are no equivalent excitations possible; the largest valence-shell correlations are associated with bivirtual[10] excitations, generally weaker than internal ones, and partially canceled by similar threshold excitations. For these reasons we expect triple and quadruple excitation contributions to the EA to be suppressed as compared to Cu^-, Cu, where they contribute[7] about 0.2 eV; we chose not to include such effects here. Since Zn^- ^4S and ^4P are expected to behave similarly with respect to their thresholds, no further core or higher excitations were examined for them either.

Using the correlated (N-shell) results for Zn^- ^4P and Zn^- $^4S^\circ$, we obtain an oscillator strength of 0.323 (length) and 0.287 (velocity) for the $^4P \rightarrow {}^4S^\circ$ transition using the theoretical energy. If we use the experimental[27] energy for the thresholds ($J=0 \rightarrow J=0$) and the final theoretical estimate for the electron affinities [$J=\frac{1}{2}$ to $J=\frac{3}{2}$], the length result becomes 0.342 and the velocity 0.272. For comparison, the RHF results (theoretical energy) are 0.401 (length) and 0.208 (velocity). Throughout, the effects of nonorthonormality have been treated[21] exactly.

IV. RELATIVISTIC THEORY

A good sampling of relativistic theory and how it is applied to atoms may be found in recent conference proceedings.[28–31] We follow current practice and take as a relativistic Hamiltonian for N electrons,

$$H_{\text{rel}} = \sum_{i=1}^{N} [c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + \beta_i c^2 + V_N(r_i)] + \sum_{\substack{i,j \\ (i<j)}} r_{ij}^{-1} + \sum_{\substack{i,j \\ (i<j)}} \left[\frac{-\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{p}_i)(\boldsymbol{\alpha}_j \cdot \mathbf{p}_j)}{2} r_{ij} \right] , \tag{1}$$

α and β are[32] Dirac 4×4 matrices, c is the speed of light, and V_N is the electron-nuclear potential, which if pointlike would be $-Z/r_i$. V_N can[33] also be obtained by a finite proton-charge distribution, which is either a constant (our choice) or given by the Fermi distribution.[33] (For binding energies of innermost electrons, quantum-electrodynamical effects can be significant.[34]) The first three terms represent the Dirac Hamiltonian for the one-electron problem, while the fourth is the Coulomb repulsion. The last two terms constitute the Breit Hamiltonian, of which the first is called[32] the magnetic and the second the retardation contribution; these represent approximate two-particle relativistic corrections. We generate a zeroth-order function using the first four operators (i.e., without the Breit corrections) and an approximate wave function which is a linear combination of determinants whose elements are spinors, $\phi_{n\kappa m}(r)$. The one-electron spinors satisfy[32] the following eigenvalue equations:

$$\begin{aligned} \hat{j}^2 \phi_{n\kappa m} &= j(j+1)\phi_{n\kappa m} , \\ \hat{j}_z \phi_{n\kappa m} &= m\phi_{n\kappa m} , \\ \hat{K} \phi_{n\kappa m} &= \kappa \phi_{n\kappa m} , \end{aligned} \tag{2}$$

where $\hat{K} = \beta(\underline{1} + \underline{\sigma} \cdot \underline{l})$, and $\underline{\sigma}$ is the 2×2 Pauli matrix.

As is usual, we seek to reduce matrix elements between these determinants (or linear combinations of them) to linear combinations of one- and two-particle radial integrals. One can do this directly by applying the Slater-Condon rules (the spinors form an orthonormal set) and then performing the angular integrations.

It is for this last area that the work of Grant is so important; in particular, two of his papers.[35,32] For us, the most important difference between the two lies in which representation is emphasized: uncoupled[35] or coupled.[32] Although there are many advocates of coupled representations [nonrelativistically and relativistically], we find them not overly useful due to (1) the great variety of configurations encountered, (2) the need to keep all, or nearly all, couplings except in special cases like those discussed for REDUCE, and (3) the algebraic and programming complexities introduced.

The spinors are represented as

$$\phi_{n\kappa m}(\mathbf{r}) = \frac{1}{r} \begin{bmatrix} P_{n\kappa}(r) & X_{\kappa,m}(\Omega,s) \\ iQ_{n\kappa}(r) & X_{-\kappa,m}(\Omega,s) \end{bmatrix} . \tag{3}$$

Since P and Q do not depend on m, we are using a "restricted" form of the theory.

We write

$$X_{\kappa,m} = (-1)^{l-1/2-m} \sqrt{2j+1} \sum_{m_l,m_s} \begin{pmatrix} \frac{1}{2} & l & j \\ m_s & m_l & -m \end{pmatrix} \times Y_{lm_l}(\Omega) \eta_{m_s}(s) . \tag{4}$$

These are like Grant's[35] Eqs. (3) and (4), except our X differs in phase due the differing order of coupling $\underline{s}$ and $\underline{l}$. The ( ) is a Wigner $3j$ symbol.[36]

Since $\kappa = -(j+\frac{1}{2})a$ with

$$a = \begin{cases} +1 & \text{when } l = j - \frac{1}{2} \\ -1 & \text{when } l = j + \frac{1}{2} , \end{cases} \tag{5}$$

we see that

$$\hat{l}^2 X_{\kappa,m} = l(l+1) X_{\kappa,m} \tag{6}$$

but that $X_{-\kappa,m}$ has a different eigenvalue. Also, in Eq. (3), P will turn out to be the "major" component (i.e., larger for electronlike solutions) and Q the "minor" component.

A. One- and two-particle energy matrix elements

The angular integrations can be performed using results found in standard textbooks such as Edmonds[36] and techniques discussed in Ref. 37.

We find the "overlap" integral given by

$$\langle n\kappa m \mid n'\kappa' m'\rangle = \delta_{\kappa,\kappa'}\delta_{m,m'}\int_0^\infty dr\,(P_{n\kappa}P_{n'\kappa}+Q_{n\kappa}Q_{n'\kappa}) \; . \tag{7}$$

Radial orthonormality is imposed later. Of the first three operators in H_{rel}, only $c\boldsymbol{\alpha}\cdot\boldsymbol{p}$ requires some effort to evaluate. Since its reduction is well known (e.g., Sec. 6.2 of Ref. 32), we quote the result,

$$\begin{aligned}\langle n\kappa m \mid c\boldsymbol{\alpha}\cdot\mathbf{p}+\beta c^2+V_N(r)\underline{1} \mid n'\kappa' m'\rangle &\equiv I(n\kappa m, n'\kappa' m') \\ &= \delta_{\kappa,\kappa'}\delta_{m,m'}c\left\{\int_0^\infty \left[Q_{n'\kappa}\left[\frac{d}{dr}+\frac{\kappa}{r}\right]P_{n\kappa} - P_{n'\kappa}\left[\frac{d}{dr}-\frac{\kappa}{r}\right]Q_{n\kappa}\right.\right. \\ &\qquad \left.\left. + c\,(P_{n'\kappa}P_{n\kappa}-Q_{n\kappa}Q_{n'\kappa}) + V_N(r)(P_{n'\kappa}P_{n\kappa}+Q_{n'\kappa}Q_{n\kappa})\right] dr\right\} \; .\end{aligned} \tag{8}$$

This may be compared to Grant's[32] Eq. (6.17) for the diagonal case. The above expression contains the rest energy, which in these units (a.u.) is $c^2\int_0^\infty dr\,(P_{n'\kappa}P_{n\kappa}+Q_{n'\kappa}Q_{n\kappa})\delta_{n',n}$ and is sometimes removed.

The electrostatic matrix element may be evaluated by expressing r_{12}^{-1} as sums of products of one-electron functions using the spherical harmonic addition theorem,[37] with the result that

$$\begin{aligned}&\langle n_a\kappa_a m_a(1) n_b\kappa_b m_b(2) \mid r_{12}^{-1} \mid n_c\kappa_c m_c(1) n_d\kappa_d m_d(2)\rangle \\ &\qquad = \delta_{m_a+m_b,m_c+m_d}\left[\sum_{t\geq |m_a-m_c|}^{\infty} d^t(j_a m_a; j_c m_c)\, d^t(j_d m_d; j_b m_b)\, R^t(n_a\kappa_a n_b\kappa_b; n_c\kappa_c n_d\kappa_d)\right] ,\end{aligned} \tag{9}$$

where

$$d^t(jm;j'm') = \left[\sqrt{(2j+1)(2j'+1)}\,(-1)^{j+j'+m+1/2}\begin{bmatrix} j & j' & t \\ \frac{1}{2} & -\frac{1}{2} & 0\end{bmatrix}\begin{bmatrix} j & j' & t \\ -m & m' & m-m'\end{bmatrix}\right] , \tag{10}$$

with

$$t+j+j' \begin{cases} \text{even if } a\neq a' \\ \text{odd if } a=a' \; , \end{cases}$$

and

$$\begin{aligned} R^t(n_a\kappa_a n_b\kappa_b; n_c\kappa_c n_d\kappa_d) = \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{r_<^t}{r_>^{t+1}} &[P_{n_a\kappa_a}(1)P_{n_c\kappa_c}(1)+Q_{n_a\kappa_a}(1)Q_{n_c\kappa_c}(1)] \\ &\times [P_{n_b\kappa_b}(2)P_{n_d\kappa_d}(2)+Q_{n_b\kappa_b}(2)Q_{n_d\kappa_d}(2)] \; ,\end{aligned} \tag{11}$$

which may be compared to Grant's[32] Eqs. (7.11) [a sum over ν should be present], (7.12), (6.2), and (6.5). As has been noted,[35] two symmetries exist:

$$d^t(j'm';jm) = (-1)^{-m+m'} d^t(jm;j'm') \tag{12a}$$

and

$$d^t(j,-m;j',-m') = -(1)^{j+j'+t} d^t(jm;j'm') \; . \tag{12b}$$

For the general magnetic two-particle integral, the result we desire follows immediately by insertion of the expansion of r_{12}^{-1} and direct evaluation of the one-particle integrals. We obtain

$$\left\langle n_a\kappa_a m_a(1)n_b\kappa_b m_b(2)\left|\frac{-\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2}{r_{12}}\right|n_c\kappa_c m_c(1)n_d\kappa_d m_d(2)\right\rangle$$

$$=2\delta_{m_a+m_b;m_c+m_d}(-1)^{m_c-m_b}\sum_{q=-1}^{+1}\sum_{p\geq 0}[H_1H_3R_1+H_2H_4R_2-H_1H_4R_3-H_2H_3R_4]\ , \quad (13)$$

where the different H's are expressed in terms of the general angular momentum coefficient,

$$h_q^p(ljm;l'j'm')=\sqrt{3(2j+1)(2j'+1)(2l+1)(2l'+1)}\begin{pmatrix} l & p & l' \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times\sum_{m_s=-1/2}^{+1/2}\begin{pmatrix} \frac{1}{2} & l & j \\ m_s & m-m_s & -m \end{pmatrix}\begin{pmatrix} \frac{1}{2} & l' & j' \\ m_s+q & -q-m_s+m' & -m' \end{pmatrix}$$

$$\times\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 1 \\ m_s & -m_s-q & q \end{pmatrix}\begin{pmatrix} l & p & l' \\ m_s-m & q+m-m' & -q+m'-m_s \end{pmatrix}\ . \quad (14)$$

Here,

$$\begin{aligned} H_1&=h_q^p(l_c^*j_cm_c;l_aj_am_a)\ ,\\ H_2&=h_q^p(l_cj_cm_c;l_a^*j_am_a)\ ,\\ H_3&=h_q^p(l_bj_bm_b;l_d^*j_dm_d)\ ,\\ H_4&=h_q^p(l_b^*j_bm_b;l_dj_dm_d)\ , \end{aligned} \quad (15)$$

for which l^* signifies the l of the minor component.

The general radial integral is

$$R_M^p(il;jm)=\int_0^\infty\int_0^\infty dr\,ds\,P_{n_i\kappa_i}(r)Q_{n_j\kappa_j}(r)$$

$$\times\frac{r_<^p}{r_>^{p+1}}P_{n_l\kappa_l}(s)Q_{n_m\kappa_m}(s)\ , \quad (16)$$

with

$$\begin{aligned} R_1&=R_M^p(ab;cd),\quad R_3=R_M^p(ad;cb)\ ,\\ R_2&=R_M^p(cd;ab),\quad R_4=R_M^p(cb;ad)\ . \end{aligned} \quad (17)$$

These equations are closely related to Grant's[35] Eqs. (36) and (37). In our opinion, this form of the result is most easily programmed, as it has the lowest-order nj symbols ($3j$), without an increase in the number of summations present. This form can also be easily stored and recovered when required.

The various restrictions on p, q, and m_s follow from the properties of $3j$ symbols.[36] From Eq. (14) we have

$$|l-l'|\leq p\leq l+l'\ ,$$

i.e.,

$$\begin{aligned} &p=|l-l'|,\ \ |l-l'|+2,\ldots,l+l'\ ,\\ &|m_s+q|=\tfrac{1}{2}\ ,\\ &|-q-m_s+m'|\leq l'\ ,\\ &|q+m-m'|\leq p\ ,\\ &|m-m_s|\leq l\ . \end{aligned} \quad (18)$$

We also have the symmetries

$$h^p_{-q}(l\,j-m;l'j',-m')$$

$$=(-1)^{l+l'+j+j'+1}h_q^p(ljm;l'j'm')$$

and

$$h_q^p(l'j'm';ljm)=h^p_{-q}(ljm;l'j'm')\ . \quad (19)$$

These allow us to require $q\geq 0$ and $m<0$. We have the single radial symmetry

$$R_M^p(il;jm)=R_M^p(li;mj)\ . \quad (20)$$

We plan to discuss retardation algebra in a later paper. Generally, retardation effects are 10% of the magnetic ones; here, at most, we will be concerned with the average retardation energy which has been adequately discussed by Grant.[35]

B. Formation of N-electron angular momentum eigenstates

As in the nonrelativistic case,[9,10] we will expand our approximate N-electron wave function in eigenstates of angular momentum. This naturally leads to the introduction of the configuration, which relativistically is expressed in terms of the occupancies q of the relativistic subshells nlj. Here l is to be associated with the major component. A subshell is closed if $q=2j+1$, i.e., all possible values of m_j are present. The necessity of having the radial functions depend on j is the cause of much of the additional complication associated with relativistic treatments.

Since the total energy is independent of M, we fix its value at $+J$. We then create all determinants associated with the chosen configuration; eigenstates of $\hat{J}^2$ are developed by setting up the $\hat{J}^2$ matrix and diagonalizing it. Since the one- and two-particle matrix elements needed to do this are straightforward results of angular momentum theory, they will not be given here. Often there may be more than one eigenvector; these may be distinguished by requiring that a subshell or group of subshells be eigenstates of $\hat{j}^2$ operators which operate only in the subspace of their spinors, and this process may be done simultaneously, i.e., we set up the matrix for the operator,

$$\sum_{i=1}^{M} \alpha_i \hat{j}_i^{\,2} ,$$

and wish to find the eigenvalues

$$\sum_{i=1}^{M} \alpha_i j_i (j_i + 1) , \tag{21}$$

where the α_i are constants chosen to ensure the eigenvalues are distinct ($\alpha_1 = 2.5 \times 10^3$, $\alpha_2 = 50$, $\alpha_3 = 1$ often work well for $M = 3$) and $i = 1$ always corresponds to the full group. The benefits of creating parents, which we have done nonrelativistically as well,[9,10] include simplified analyses of the final results, simplified off-diagonal matrix element structure, and the possibility of discarding certain eigenvectors, if desired. It may perhaps appear that we have returned to the coupled representation (e.g., Ref. 32)—but this imposes a particular coupling, whereas our process allows the user to determine any coupling, including none (uncoupled representation), at the time that the calculation is done.

As an illustration, let us consider the real problem of Zn^- $3d^9 4s 4p^3$ "^6D"$_{1/2}$. The designation of L and S is, of course, approximate, so we ignore it for the moment. Let us restrict ourselves to the zeroth-order configuration, which is just used to label the state. Since the closed subshells make no contribution to angular momentum matrices, we need focus only on the specified open subshells. If we take into account relativity and specify the J's of the various subcouplings where necessary, the following relativistic configurations contribute to the above state:

$$\begin{aligned}
&(\mathrm{i})\ d^4_{3/2} d^5_{5/2} S_{1/2} p^3_{3/2} ,\\
&(\mathrm{ii})\ d^4_{3/2} d^5_{5/2} S_{1/2} p^2_{1/2} p_{3/2} ,\\
&(\mathrm{iii})\ (d^4_{3/2} d^5_{5/2} S_{1/2})(2)[p_{1/2} p^2_{3/2}(2)](3/2) ,\\
&(\mathrm{iv})\ (d^4_{3/2} d^5_{5/2} S_{1/2})(2)[p_{1/2} p^2_{3/2}(2)](5/2) ,\\
&(\mathrm{v})\ (d^4_{3/2} d^5_{5/2} S_{1/2})(3)[p_{1/2} p^2_{3/2}(2)](5/2) ,\\
&(\mathrm{vi})\ d^3_{3/2} d^6_{5/2} S_{1/2})(2) p^3_{3/2} ,\\
&(\mathrm{vii})\ (d^3_{3/2} d^6_{5/2} S_{1/2})(2) p^2_{1/2} p_{3/2} ,\\
&(\mathrm{viii})\ (d^3_{3/2} d^6_{5/2} S_{1/2})(2)[p_{1/2} p^2_{3/2}(2)](3/2) ,\\
&(\mathrm{ix})\ (d^3_{3/2} d^6_{5/2} S_{1/2})(2)\,|\,p_{1/2} p^2_{3/2}(2)\,|\,(5/2) ,\\
&(\mathrm{x})\ (d^3_{3/2} d^6_{5/2} S_{1/2})(1) p^3_{3/2} ,\\
&(\mathrm{xi})\ (d^3_{3/2} d^6_{5/2} S_{1/2})(1) p^2_{1/2} p_{3/2} ,\\
&(\mathrm{xii})\ (d^3_{3/2} d^6_{5/2} S_{1/2})(1)[p_{1/2} p^2_{3/2}(0)](1/2) ,\\
&(\mathrm{xiii})\ (d^3_{3/2} d^6_{5/2} S_{1/2})(1)[p_{1/2} p^2_{3/2}(2)](3/2) .
\end{aligned} \tag{22}$$

There are a number of important points connected with the above: (1) a single nonrelativistic configuration has exploded to 13 relativistic ones, (2) the numbers in parentheses give the value of J imposed on the subconfiguration (obviously, the choice of subcouplings is not unique), (3) our interest in the zeroth order is in the linear combination of the 13 couplings which gives the lowest energy, (4) if the result were pure LS, couplings (iv), (v), (ix), and (xii) would not be present, and (5) just as in the nonrelativistic case, not all values of J are possible for equivalent electrons $(nlj)^q$. Grant[32] gives us a list of the allowed values in his Table II. One way[38] to derive these is to look at the normalization integral for a $\hat{J}^{\,2}$ eigenvector. Judd[39] gives us such wave functions [Eqs. (1.20) and (3.1)] for groups of two and three electrons. Using this, we find the general conditions

$$J \text{ even} \tag{23}$$

for two electrons, and

$$-(2J_{12}+1)^{-1} + 2(-1)^{2J} \begin{Bmatrix} J_{12} & j & J \\ J_{12} & j & j \end{Bmatrix} \neq 0 \tag{24}$$

for three electrons, where $J_{12} < 2j$ and is even. The { } in (24) is a Wigner $6j$ symbol.[36] Using (24) we can show $J \neq 3j$, $3j-1$, $3j-2$, $3j-4$, and 1/2. These results are all consistent with Grant's[32] Table II. We note that Eq. (24) is not capable of predicting how many survivors there are for each (j,J) pair due[38] to linear dependencies associated with Eq. (3.1) of Judd.[39]

Formation of approximate $\hat{L}^{\,2}, \hat{S}^{\,2}$ eigenstates

It would be useful to generate approximate $\hat{L}^{\,2}, \hat{S}^{\,2}$ eigenstates solely from angular momentum theory. This would provide estimates for the weights of the relativistic configurations as input for such procedures[33] as the multiconfiguration Dirac-Fock procedure (MCDF), and provide a valuable way of analyzing the results. Since purely angular momentum treatments require no knowledge of the radial functions, we must eliminate this dependence from the exact problem. We do so by setting all minor components to zero, and assume the major components are independent of j. With these conditions (cf. Bessis *et al.*[40]) we diagonalize the matrix associated with the operator

$$\sum_{i=1}^{M} (\alpha_i \hat{j}_i^{\,2} + \beta_i \hat{l}_i^{\,2} + \gamma_i \hat{S}_i^{\,2}) , \tag{25}$$

where α_i, β_i, and γ_i are constants chosen to separate the eigenvalues. Frequently we only want an $\hat{l}^{\,2}, \hat{S}^{\,2}$ eigenvalue for the whole group; this can be achieved with $\beta_i = \gamma_i = 0$, $i > 1$. The matrix elements have been set up by using $\underline{l} = \underline{j} - \underline{s}$; since $\langle X_{\kappa,m} \,|\, \hat{S}_- X_{\kappa',m'} \rangle = \langle \hat{S}_+ X_{\kappa m} \,|\, X_{\kappa' m'} \rangle$ we need only know how $\hat{S}_+$ and $\hat{S}_z$ operate on $X_{\kappa,m}$. This can be easily deduced from Eq. (4).

C. Interactions of one electron and a closed subshell

Extending the work of Grant[32] to the off-diagonal case, we introduce the core-valence energy g_{CV},

$$g_{\mathrm{CV}} = \sum_{a \in \mathrm{core}} \langle i(1) a(2) \,|\, g_{12}(1 - P_{12}) \,|\, i'(1) a(2) \rangle ,$$

where the sum is over spinors a belonging to closed subshells only ($2j_a + 1$ of them for each subshell), and where for the electrostatic operator we obtain

$$g_{\mathrm{CV}}(c)=\delta_{\kappa_i\kappa_{i'}}\delta_{m_im_{i'}}\sum_{\substack{n_A\kappa_A\\ \text{(closed)}}}(2j_{A+1})\left[R^0(n_i\kappa_{i'}n_A\kappa_A;n_{i'}\kappa_{i'}n_A\kappa_A)-\sum_t\begin{pmatrix} j_i & j_A & t\\ \frac{1}{2} & -\frac{1}{2} & 0\end{pmatrix}^2 R^t(n_i\kappa_{i'}n_A\kappa_A\cdot n_A\kappa_A\cdot n_{i'}\kappa_i)\right] . \tag{26}$$

Here, $|l_i-l_A|\le t\le l_i+l_A$ in steps of 2 and l refers to the major component; we must also satisfy $|j_i-j_A|\le t\le j_i+j_A$ in steps of 1. We can see that from an angular viewpoint, $g_{\mathrm{CV}}(c)$ behaves as a one-particle operator and also that the off-diagonal result is the logical extension of the diagonal case available from Grant.[32,35] We obtain for the magnetic core-valence contributions,

$$g_{\mathrm{CV}}(M)=\delta_{m_im_{i'}}\delta_{\kappa_i\kappa_{i'}}\sum_{\substack{n_a\kappa_a\\ \text{(closed)}}}(2j_a+1)\sum_p\left[\begin{pmatrix} j_i & j_a & p\\ \frac{1}{2} & -\frac{1}{2} & 0\end{pmatrix}^2[R_M^p(ia;ai')+R_M^p(ai';ia)]\right.$$

$$\left.+\Gamma^p_{j_ij_al_i}R_M^p(ii';aa)+\Gamma^p_{j_ij_al_i^*}R_M^p(aa;ii')\right] , \tag{27a}$$

where

$$\Gamma^p_{jj'l}=\delta_{l,j+(1/2)}\left[\frac{j}{j+1}\begin{pmatrix} j & j' & p\\ \frac{1}{2} & -\frac{1}{2} & 0\end{pmatrix}^2+\frac{(2j+3)}{(j+1)}\begin{pmatrix} j+1 & j' & p\\ \frac{1}{2} & -\frac{1}{2} & 0\end{pmatrix}^2\right]$$

$$+\delta_{l,j-(1/2)}\left[\frac{j+1}{j}\begin{pmatrix} j & j' & p\\ \frac{1}{2} & -\frac{1}{2} & 0\end{pmatrix}^2+\frac{(2j-1)}{j}\begin{pmatrix} j-1 & j' & p\\ \frac{1}{2} & -\frac{1}{2} & 0\end{pmatrix}^2\right] , \tag{27b}$$

and

$a_i=a_a$, j_i+j_a+p even

$a_i\ne a_a$, j_i+j_a+p odd .

For the diagonal case, this reduces to Grant's result[32] with the overall sign corrected [as implied by his Eq. (8.34)] if one makes use of the symmetry relation derived here: $\Gamma^{aa'}_{jpj'}(a)=\Gamma^{a'a}_{j'pj}(-a')$ for $a'=a$ ($j+j'+p$ is then even) and the radial symmetry $G_M^{p;\pm 1}(A,B)=G_M^{p;\mp 1}(B,A)$, where $G_M^{p;+1}(A,B)=R_M^p(AA;\ BB)$ and $G_M^{p;-1}(A,B)=R_M^p(BB;AA)$.

One of the few independent checks of relativistic results involves examining the results in the nonrelativistic limit. Formally, we can do this by setting the minor components equal to zero and taking the major components to be independent of j (see the work of Huang *et al.*[41] for possible computational problems in taking nonrelativistic limits).

Let us make such a comparison for the average energy,[42] which can be obtained from g_{CV} by taking $i'=i$ and multiplying Eqs. (26) and (27) by $2j_i+1$, yielding Eqs. (8.33) and (8.34) of Grant[32] [after the sign correction is made to (8.34)]. We have tabulated the average electrostatic energy per closed shell pair in Table III.

Let us consider the nonrelativistic limit for a pair of equivalent p electrons. For a closed subshell, $\frac{1}{3}(2)$ of the electrons are in $p_{1/2}$ and $\frac{2}{3}(4)$ in $p_{3/2}$. Thus we wish to form $\frac{1}{15}[\frac{1}{2}(2\times 1)g_{\mathrm{av}}(p_{1/2},p_{1/2})+\frac{1}{2}(4\times 3)g_{\mathrm{av}}(p_{3/2},p_{3/2})+(4\times 2)g_{\mathrm{av}}(p_{1/2},p_{3/2})]$, and let $p_{1/2}\to p_{3/2}\to p$ where there are 15 pairs of electrons in all. We obtain

$$\tfrac{1}{15}(1+6+8)F_c^0(p,p)+\tfrac{1}{15}(-\tfrac{6}{15}-\tfrac{8}{10})F^2(p,p)$$

$$=F_c^0(p,p)-\tfrac{2}{25}F_c^2(p,p) ,$$

which agrees with Slater's nonrelativistic result.[43] In the last equation the relation $G^\kappa(a,a)=F^\kappa(a,a)$ was used.

D. Future theoretical developments

The relativistic formalism has been[44] automated in a code called RELCOR. This sets up all the angular momentum eigenstates and produces relativistic energy matrix element "structure tables." We are now combining this with routines which will do the required radial integrations, and these routines will then be used to perform relativistic configuration-interaction (RCI) calculations. Development of the algebra and programming of the retardation operator is also underway.

Although the Zn$^-$ states can be considered simple, we have seen that there are a considerable number of configurations associated with just the zeroth-order function. Based on our experience[45] with Mn$^-$, it is probable that zeroth-order functions of more than 100 configurations will become routine. Problems of this size were clearly not originally anticipated.[33] The "correlating configurations" will involve an even larger N-electron basis, and it seems clear that something like the relativistic equivalent of REDUCE will have to be included from the beginning.

TABLE III. Average electrostatic energy for a pair of spinors, g_{av}.

	Equivalent electrons[a]
s	$F_c^0(s,s)$
$p_{1/2}$	$F_c^0(p_{1/2},p_{1/2})$
$p_{3/2}$	$F_c^0(p_{3/2},p_{3/2})-\frac{1}{15}F_c^2(p_{3/2},p_{3/2})$
$d_{3/2}$	$F_c^0(d_{3/2},d_{3/2})-\frac{1}{15}F_c^2(d_{3/2},d_{3/2})$
$d_{5/2}$	$F_c^0(d_{5/2},d_{5/2})-\frac{8}{175}F_c^2(d_{5/2},d_{5/2})-\frac{4}{105}F_c^4(d_{5/2},d_{5/2})$
	Nonequivalent electrons
ss'	$F_c^0(s,s')-\frac{1}{2}G_c^0(ss')$
$sp_{1/2}$	$F_c^0(sp_{1/2})-\frac{1}{6}G_c^1(s,p_{1/2})$
$sp_{3/2}$	$F_c^0(sp_{3/2})-\frac{1}{6}G_c^1(s,p_{3/2})$
$sd_{3/2}$	$F_c^0(sd_{3/2})-\frac{1}{10}G_c^2(sd_{3/2})$
$sd_{5/2}$	$F_c^0(s,d_{5/2})-\frac{1}{10}G_c^2(sd_{5/2})$
$p_{1/2}p'_{1/2}$	$F_c^0(p_{1/2},p'_{1/2})-\frac{1}{2}G_c^0(p_{1/2},p'_{1/2})$
$p_{1/2}p_{3/2}$	$F_c^0(p_{1/2},p_{3/2})-\frac{1}{10}G_c^2(p_{1/2},p_{3/2})$
$p_{1/2}d_{3/2}$	$F_c^0(p_{1/2},d_{3/2})-\frac{1}{6}G_c^1(p_{1/2},d_{3/2})$
$p_{1/2}d_{5/2}$	$F_c^0(p_{1/2},d_{5/2})-\frac{1}{14}G_c^3(p_{1/2},d_{5/2})$
$p_{3/2}p'_{3/2}$	$F_c^0(p_{3/2},p'_{3/2})-\frac{1}{4}G_c^0(p_{3/2},p'_{3/2})-\frac{1}{20}G_c^2(p_{3/2},p'_{3/2})$
$p_{3/2}d_{3/2}$	$F_c^0(p_{3/2},d_{3/2})-\frac{1}{60}G_c^1(p_{3/2},d_{3/2})-\frac{9}{140}G_c^3(p_{3/2},d_{3/2})$
$p_{3/2}d_{5/2}$	$F_c^0(p_{3/2}d_{5/2})-\frac{1}{10}G_c^1(p_{3/2},d_{5/2})-\frac{1}{35}G_c^3(p_{3/2},d_{5/2})$
$d_{3/2}d_{5/2}$	$F_c^0(d_{3/2},d_{5/2})-\frac{1}{70}G_c^2(d_{3/2},d_{5/2})-\frac{1}{21}G_c^4(d_{3/2},d_{5/2})$
	$F_c^K(a,b)=R^K(ab;ab)$[a]
	$G_c^K(a,b)=R^K(aa;bb)$

[a] See Eq. (11).

V. APPLICATIONS OF RELATIVISTIC THEORY

In this work relativistic effects are treated by performing MCDF calculations[33] with the zeroth-order function, which is taken to be the relativistic configurations generated from the single nonrelativistic configuration used to label the state. For all calculations the correct (i.e., nonaverage) electrostatic energy was used, and the use of the correct magnetic Breit energy was investigated. Our automated program is capable of producing correct (level-dependent) magnetic structure. The Breit contribution, which included[33] the average retardation energy, was usually evaluated after the zeroth-order wave function was obtained, using first-order perturbation theory. However, we did explore the use of the average Breit energy during the energy matrix diagonalization, i.e., during determination of the configurational coefficients.

In addition to modifying the MCDF program[33] to carry out the above procedure, we made three other changes. (i) Self-consistency thresholds [TESTE and TESTY in subroutine INMUAT] were reduced by an order of magnitude, so that the two ways[33] of computing the total energy yielded results agreeing to within 10^{-5} a.u. (ii) Due to the large numbers (>100) of nonaverage Coulomb integrals, the *NRE* array was overflowing in subroutine LIRFGR. We stopped incrementing it once it approached the integer size limits (all values above 2 are indistinguishable). (iii) In our copy of the MCDF code there was an error in subroutine MUATCO associated with the test for identical non-average electrostatic F and G integrals. We removed $+NFG$ from both $IJLMK$ arguments. This problem was detected by comparing the total energy (without the Breit contribution) to the CI eigenvalue (last iteration); they should agree.

In Table IV we present our results for the fine structure of the Zn^- states. All calculations were done at the zeroth-order level with the MCDF code;[33] only the average Breit contribution was used, and it was always added after the wave functions were completely determined. Several things are evident: (1) All fine-structure levels are bound (compare to Tables I and II), (2) the retardation contributions are tiny and even the average Breit contributions are of marginal importance (also, see below), and (3) all states are fairly pure ($\geq 90\%$). Here we have defined the purity to be the overlap integral between the perfect L-S eigenvector (see Sec. IV B) and the MCDF eigenvector. It is possible, of course, to analyze what LS couplings other than the dominant one appear. For example, the MCDF, "$6D$"$_{9/2}$ solution is an admixture of ^6D, $^2G(2)$, $^4F(2)$, and $^4G(1)$. The amount of each LS species present could also be obtained from overlap integrals. The relative lifetimes might be assumed proportional to $1/[1-(\text{purity})]^2$, as the denominator is a measure of the % admixture of open channels. On this basis, for Zn^- ^6D, $J=9/2$ would be thought to have the longest lifetime and $J=3/2$ the shortest. However, as noted earlier, lifetimes may involve many-body and relativistic effects, and so one should be cautious about pursuing the argument too far. For reference, the $^5D_4$ threshold was found to be 97.89% pure, with a 1.7% $^5F_4$ admixture. The $^3P_0^\circ$ involves only one relativistic configuration in zeroth order, and so it is 100% pure.

Included in Table IV is the fine structure for Zn $4p^2\,{}^3P_J$. We predict the position of the $J=2$ level, which

TABLE IV. Fine structure (via MCDF) and *LS* purity of Zn$^-$ states.

LS	*J*	Fine structure (eV) Magnetic	 Retardation	Total	*LS* purity (%)
$^6D^\circ$	9/2	0.0	0.0	0.0	99.993
$^6D^\circ$	7/2	−0.003	−0.0007	0.103	91.84
$^6D^\circ$	5/2	−0.008	−0.0019	0.165	90.83
$^6D^\circ$	3/2	−0.014	−0.0030	0.240	89.92
$^6D^\circ$	1/2	−0.020	−0.0046	0.300	97.86
4*P*	1/2	0.0	0.0	0.0	99.9904
4*P*	3/2	−0.0002	−0.000 01	0.0127	99.9989
4*P*	5/2	−0.0006	−0.000 03	0.0326	99.9949
4*S*°	3/2	0.0	0.0	0.0	99.976
^3P	0			0.0	99.910
				0.0	
^3P	1			0.0237	
				0.0271[a]	
^3P	2			0.0639[a]	

[a] Reference 27.

appears to be[27] unknown. As can be seen, the position of the $J=1$ level is in reasonable agreement with experiment.[27] To the extent that fine structure can be ascribed to a single-particle operator (i.e., the low-*Z* Pauli approximation is not useless; see Blume and Watson[46] for a formal analysis within the low-*Z* Pauli approximation and Condon and Shortley[47] for exceptions where two-particle effects play a major role), improvements will be mainly associated with single excitations of the zeroth-order function. If these behave as they do nonrelativistically, a good first-order correlation function involving single and pair excitations from core subshells will be required. Production of such results for systems of this size present a significant computational challenge.

For Zn$^-$ $^6D_{9/2}$ the effect of using the correct magnetic Breit structure was explored; the result was that the total energy was 0.0015 eV more negative. This may seem inconsistent with the results of Cheng *et al.*[48] for $1s^{\kappa}2s^{l}2p^{m}$ configurations, but is quite reasonable if it is realized that both involve just R_M from the open subshells and that for Zn$^-$, such integrals with 3*d*, 4*s*, and 4*p* arguments are individually about 10^{-6} a.u. in magnitude. Explicit calculation demonstrates that this is also the case for Zn$^-$ ^4P. Since the integrals were found to be individually so small, nonaverage effects were ignored for all other levels.

Because of the closeness of the $3d^94s4p^2\,{}^5D$ and ^5F at the RHF level (the ^5F is 0.217 eV higher) we had some concern that differential magnetic Breit effects could have a significant effect in determining MCDF zeroth-order wave functions and energies. To account approximately for this we decided to allow average magnetic Breit effects to appear in the CI matrix. Nonaverage effects were excluded because of their absolute smallness, and we did not feel that any correction would be large enough to warrant inclusion of the Breit terms directly in the MCDF equations. Corrections to the diagonal matrix element due to the addition of the Breit correction ranged from −4.2% to +15% (i.e., this is the effect on diagonal energy differences between adjacent configurations). However, the largest corrections occurred for small off-diagonal matrix elements (which have no average Breit contribution, and so remain unchanged). The net result on the total energy is an increase of 2.5×10^{-5} eV; for $^6D_{9/2}$ the effect was a rise of 5.4×10^{-6} eV. Although in this case the effect was negligible, it probably should continue to be analyzed in future calculations whenever there are "nearby" configurations or eigenstates.

Finally, while the reduction of the number of relativistic configurations in the zeroth order by, e.g., restricting the subcouplings to those accessible nonrelativistically prior to the MCDF calculation may seem attractive, it may not allow for full departure from *LS* coupling even at the zeroth-order level. Instead, our approach is to "re-dimension" the algorithms to handle all possible couplings.

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