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Relativistic modifications of charge expansion theory

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We examine the effects of relativity on the high-Z (where Z denotes nuclear charge) behavior of isoelectronic sequences and the modifications required of the traditional charge expansion theory. We propose that the idea of a complex be refined to include hydrogenic angular-momentum degeneracy, so that a relativistic complex should be defined as the set of all configurations with the same occupation of angular-momentum quantum numbers j as well as the same principal quantum numbers n. This leads to asymptotic, high-Z grouping of states that might cut across the conventional LS-coupled states, grouping together levels from different configurations, as long as the n and j occupation numbers remain the same. This regrouping substantially reduces the asymptotic configuration interaction from that predicted by a nonrelativistic theory. Frequently correlation configurations that are significant in low-Z ions disappear entirely in high-Z ions.

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I. INTRODUCTION

The systematic behavior of atomic properties along an isoelectronic sequence has long been a basis for understanding atomic structure theory, permitting the prediction of atomic properties by interpolation and extrapolation along the atomic number. In general, this also provides the framework for understanding qualitative trends in the atomic structure of moderately and highly charged ions. The systematic behavior of energy levels has provided a useful spectroscopic tool for the prediction and identification of ionic energy levels [1,2]. The problem of understanding other properties, such as transition oscillator strengths, has also benefited from analyses based on isoelectronic regularities [3]. The effects of an important class of strong configuration interaction (CI), namely, the asymptotic CI, also belong to one aspect of isoelectronic sequence behavior.

The theoretical foundation of most such analyses is the charge expansion theory of Layzer [4], where the many-electron Schrödinger equation is partitioned such that one can make a perturbation expansion in descending powers of Z, the "bare" nuclear charge. Thus, for example, the nonrelativistic total energy of any state of any atom or ion can be written as

$$E=E_0Z^2+E_1Z+E_2+E_3/Z+\cdots \quad . \tag{1}$$

Here the zeroth-order energy E_0 is the sum of the hydrogenic energies of each of the electrons of the atom (ion). The first-order energy E_1 represents the leading effect of the electron-electron repulsion and the succeeding E_i's are higher-order energy coefficients of Rayleigh-Schrödinger perturbation theory. It is important to note that each of these energy coefficients is independent of Z, the only Z dependence being that explicitly indicated in Eq. (1). Similar expansions can be derived for other properties as well.

One can use the Z expansion theory to carry out calculations of atomic structures and make quantitative predictions of energy levels and other properties [5]. Such a program has proven successful for lighter systems with few electrons [6]. However, of even more importance is the fact that it provides a single comprehensive framework for understanding isoelectronic behavior. The underlying idea of this scheme is to look at an entire sequence as a single entity rather than as individual ions. From this standpoint, the atomic system is viewed as having a continuous variable Z, which can be raised or lowered at will. Real atoms or ions are described by those points where Z is an integer.

Another important feature of this scheme is the asymptotic ($Z\rightarrow\infty$) configuration interaction needed to obtain the E_1 coefficient. If there is a degeneracy in the zeroth order, then these multielectron configuration state functions will mix in the first order [4,7]. The classic example here is the ground state of the Be-like ions, where $2s^2\,{}^1S$ is asymptotically degenerate with $2p^2\,{}^1S$ and this configuration interaction persists along the entire sequence. As discussed later, this CI produces a linear Z dependence in the correlation energy.

This theoretical scheme holds out the marvelous promise of encompassing all the ions of a sequence, irrespective of the stage of ionization. It should be noted that, since the expansion is in powers of Z^{-1}, the inverse nuclear charge is the natural parameter for a graphical depiction of atomic properties [3]. With the $Z=\infty$ limit known exactly from theory [7], the $Z^{-1}=0$ point is well established and all other high-Z values are obtained by interpolation, not extrapolation. Unfortunately, this charge expansion theory is entirely nonrelativistic and the highly charged ions of greatest interest will most certainly be dominated by relativistic effects. Also, it is not

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possible to make so neat a theoretical reduction relativistically. The expansion coefficients E_i of Eq. (1) are now dependent on $Z\alpha$, where α is the fine-structure constant. However, it is still possible to make some physically reasonable conjectures as to the manner in which relativity modifies the predictions of charge expansion theory, and that is the topic addressed in this paper.

In the next section we review the nonrelativistic Z-expansion theory and present in Sec. III our arguments for the physical effects to be expected due to relativity. Section IV is devoted to examples of the relativistic modifications of energy levels and asymptotic CI. We expect relativistically that energy levels will cluster together not only according to their principal quantum number occupancy, as predicted by the nonrelativistic theory, but in addition according to the j quantum number occupancy. This further suggests that the only asymptotic CI to survive for high Z is also determined by the j occupancy. Our conclusions are presented in Sec. V.

II. NONRELATIVISTIC Z-EXPANSION THEORY

We use atomic units (a.u.) throughout this article unless stated otherwise. The conventional charge expansion theory begins with the many-electron, nonrelativistic Schrödinger equation written in terms of the scaled distance variable $\rho=Zr$. This casts the equation into a form suitable for Rayleigh-Schrödinger perturbation theory with the interelectronic repulsion as the perturbation and $1/Z$ as the perturbation parameter,

$$\left[\sum_{\mu} h_S(\rho)+\frac{1}{Z}\sum_{\mu>\nu}\frac{1}{\rho_{\mu\nu}}\right]\Psi=\mathcal{E}\Psi \ , \tag{2}$$

where the sums run over all the electrons in an atom. Here h_S is the nonrelativistic, one-electron hydrogen *atom* Hamiltonian and the eigenvalue is

$$\mathcal{E}=E/Z^2 \ , \tag{3}$$

where E is the eigenvalue of the "unscaled" Schrödinger equation.

The wave function and the total energy are then given by the expansions

$$\Psi=\Psi^{(0)}+\Psi^{(1)}/Z+\Psi^{(2)}/Z^2+\cdots \ , \tag{4}$$

$$\mathcal{E}=E_0+E_1/Z+E_2/Z^2+\cdots \ . \tag{5}$$

Because of the separable nature of $H_0,\Psi^{(0)}$ is simply the antisymmetrized product of hydrogen atom wave functions, populated according to the occupation numbers of the state under consideration. As mentioned in Sec. I, E_0 is the sum over these hydrogen atom energies and E_1 is the first-order energy coefficient

$$E_1=\langle\Psi^{(0)}|V|\Psi^{(0)}\rangle,\quad V=\sum_{\mu>\nu}\rho_{\mu\nu}^{-1} \ . \tag{6}$$

It should be emphasized that everything is evaluated with hydrogen atom wave functions, i.e., with $Z=1$. The entire Z dependence has been thrown into the power-series expansion in Z^{-1}.

If there is a degeneracy in zeroth order, it is removed by diagonalizing the first-order energy matrix over these degenerate state functions

$$V_{pq}=\langle\Phi_p^{(0)}|V|\Phi_q^{(0)}\rangle \ . \tag{7}$$

In the previous example of a Be-like ion, one diagonalizes the first-order matrix to get the zeroth-order function

$$\Psi^{(0)}=a_1\Phi(1s^22s^2)+a_2\Phi(1s^22p^2) \ , \tag{8}$$

where the coefficients a_i are the elements of the eigenvector of the E_1 matrix [Eq. (6)] and the configuration state functions $\Phi(1s^22s^2)$ and $\Phi(1s^22p^2)$ correspond to $\Phi_p^{(0)}$ and $\Phi_q^{(0)}$ in Eq. (7), respectively. The set of all configurations of the same parity that are degenerate in the hydrogenic limit (without relativistic corrections) has been called a *complex* and it is really the more appropriate designation for the states of a highly charged ion rather than any single configuration [4].

This configuration interaction within a complex, induced by the asymptotic degeneracy, has significant consequences in two important ways. First, matrix elements evaluated with the CI wave function of Eq. (8) usually are quite different from matrix elements evaluated with only one of the degenerate configuration state functions, namely, the nominal state configuration. Furthermore, experience shows that usually the mixing predicted by charge expansion theory persists along the entire isoelectronic sequence [8] at least qualitatively and can have strong effects on properties such as oscillator strengths [9].

Second, the asymptotic CI has a profound effect on the correlation energy for an isoelectronic sequence. The correlation energy is traditionally defined [10] as the difference between the exact total energy and the single-configuration Hartree-Fock energy *minus relativistic corrections.* Obviously, this is too simplistic since modern atomic structure theory can now account for most leading relativistic and quantum electrodynamic (QED) corrections. How to define a correlation energy that is consistent with the current theoretical capability is a complicated issue by itself and we shall retain the traditional definition in this article since our conclusion is not affected by adopting a more modern definition of the correlation energy.

It is known that the Hartree-Fock approximation also has a similar expansion in powers of Z^{-1}, with the same zeroth-order energy term as in Eq. (1), but with a first-order energy contribution that is the same only for the nondegenerate case [11,12]

$$E_{\mathrm{HF}}=E_0Z^2+E_1'Z+E_0'+\cdots \ , \tag{9}$$

so that the correlation energy ΔE, which is the difference between the Hartree-Fock and the exact energy, is given by an expansion

$$\Delta E=\Delta E_1Z+\Delta E_2+\Delta E_3/Z+\cdots \tag{10}$$

or, when there are no degenerate configurations in the high-Z limit,

$$\Delta E=\Delta E_2+\Delta E_3/Z+\cdots \ . \tag{11}$$

In other words, the correlation energy has a linear dependence on Z or approaches a constant asymptotic value (ΔE_2) with high Z, depending on whether or not there is an asymptotic degeneracy.

Since the zeroth-order energy is given by the sum of one-electron energies ϵ_n, the gross level ordering for high Z is determined solely by the principal quantum number occupation. This is often quite different from the level structure of the neutral atom. For example, $2p^2\,{}^1S$ is not even a bound state for neutral Be, but it quickly comes down below all of the $n=3$ levels as one moves along the sequence. Similarly, all states of $3d^3$ in the Al sequence must come down below the $3s^24l$ levels, even though $3s^24s$ is the first excited state in neutral Al. In general, all states in an isoelectronic sequence must cluster together asymptotically according to their principal quantum number occupancy. Such knowledge about the asymptotic behavior of a sequence provides a general framework for understanding the structure problem, allowing one to anticipate changes in level structure, what configuration interactions should be necessary, etc. The essential physics of the method derives from the fact that, for a highly charged ion, the nuclear central field is so strong that the structure problem is dominated by the hydrogenic character of the system, with the interelectronic repulsion truly providing only a perturbation to the level scheme. However, the dominant configuration interactions are determined by the hydrogenic degeneracy condition.

III. RELATIVISTIC ENERGY LEVELS

Unfortunately, a very strong central field produces classically very large particle velocities, especially near the nucleus. This in turn means that the system requires a relativistic description, whereas the preceding discussion has been nonrelativistic. Unfortunately, also, a fully relativistic charge expansion theory has not yet been developed and it is difficult to see how one would develop such a theory. Some attempts have been made to incorporate the lowest-order relativistic corrections [13,14], i.e., adding the one-particle Pauli operators to the Hamiltonian, which introduce terms of order $Z^4\alpha^2$ into the energy expansion [15]. However, a fully relativistic theory would in principle include all powers of Z, making the idea of a large-Z asymptote meaningless.

The problem arises from the Dirac single-particle Hamiltonian, which would have to be included in the treatment. In the conventional approach to the multielectron, relativistic structure problem, the wave equation is

$$\left[\sum_{\mu} h_D(\mu)+\sum_{\mu>\nu} 1/r_{\mu\nu}\right]\Psi=E\Psi\ , \tag{12}$$

where h_D is the hydrogenlike Dirac Hamiltonian with nuclear charge Z. However, since the Dirac Hamiltonian is linear in the momentum operator, a Z scaling of the distance variable does not lead to a separation where the interelectronic interaction can be treated as a perturbation with the resulting expansions in powers of Z^{-1}, as in the nonrelativistic theory. Indeed, since the Dirac energy ultimately diverges for a finite value of Z ($Z=137$ for a point nucleus), one should not expect a theory that permits arbitrarily large values of Z.

Nevertheless, we feel that it should be possible to describe the high-Z trends of atomic properties in terms of a relativistic modification. In analogy to the nonrelativistic scheme, due to the overwhelming nuclear central field, one should expect the structure problem to be dominated by the hydrogenic character of the system, with the interelectronic repulsion introducing a "fine tuning" of the level structures. The differences due to relativity arise from the fact that the Dirac hydrogenic energy levels depend not only on the principal quantum number, but also on the one-electron total angular momentum $j=l\pm\frac{1}{2}$,

$$\epsilon_{nj}=\alpha^{-2}\{[1+(\alpha Z/n^*)^2]^{-1/2}-1\}\ , \tag{13}$$

where α is the fine-structure constant and

$$n^*=n-(j+\tfrac{1}{2})+[(j+\tfrac{1}{2})^2-(\alpha Z)^2]^{1/2}\ . \tag{14}$$

The rest mass has been subtracted in Eq. (13) to make ϵ_{nj} consistent with the nonrelativistic one-electron energy.

We therefore suggest that one should define a relativistic complex as the set of all relativistic configurations with the same n and j occupation. For high Z, energy levels should be expected to cluster together according to their nj occupancy and to separate if the jj configurations are different, even though the principal quantum numbers are the same. We also suggest that the asymptotic configuration interaction will follow the analogous rule, which can be significantly different from the predictions of the nonrelativistic theory.

In Sec. IV we will describe the results of relativistic calculations of selected ionic structures along isoelectronic sequences. The first group of examples is designed to illustrate the relativistic modifications of the high-Z energy-level structures. The second group shows the effect of relativity on the asymptotic configuration interaction. For certain cases, it is possible for relativity to entirely remove the configuration interaction so that the high-Z wave function reverts to a single (relativistic) configuration, with the concomitant disappearance of the linear-Z behavior of the correlation energy. All the calculations were carried out both in the Pauli intermediate-coupling approximation and in the multiconfiguration Dirac-Fock (MCDF) approximation without the Breit interaction and QED corrections. The results of the Pauli approximation and the MCDF calculations were basically the same. Hence, except where otherwise noted, the results quoted will be those of the MCDF calculations. We should emphasize that these are only a few representative samples. The effects being illustrated have much broader and more far-reaching consequences.

The Breit interaction and QED corrections—better known as the Lamb shift—have a more complicated Z dependence. For instance, the leading term of the self-energy has a $(Z\alpha)^4\ln(Z\alpha)$ dependence, while that of the vacuum polarization has a $(Z\alpha)^4$ dependence [16]. The leading term of the Breit interaction also has a $(Z\alpha)^4$ dependence [16]. To avoid complication, we have omitted the Breit interaction and QED corrections from all our relativistic numerical results when they are used to elucidate qualitative aspects of the charge expansion theory. However, including appropriate Breit interaction and QED corrections in theoretical results is crucial for achieving reasonable agreements with experimental data on highly charged ions [17]. All of our relativistic calculations were carried out with extended nuclei, while nonrelativistic calculations were performed with point nuclei. The Breit interaction, which is the leading relativistic correction to the interelectronic repulsion, is usually included in MCDF calculations as a first-order perturbation. Therefore, the total energy is affected by the Breit interaction, but the wave functions are not.

IV. RESULTS OF CALCULATIONS

Figure 1 shows the computed excitation energies, within the $n=3$ complex, for the Na isoelectronic sequence. The excitation energies here have been scaled by $Z_{\mathrm{eff}}=Z-10$, which would give an effective Z of unity for neutral Na. Nonrelativistically, the separation of the $3s$, the $3p$, and the $3d$ levels should vary linearly with Z. The influence of relativity does not begin to dominate until somewhere in the vicinity of $Z=40$, i.e., about the 20th stage of ionization. For high Z the "clustering" of levels according to the relativistic complex becomes evident. The $3p_{1/2}$ level continues to "track" the $3s_{1/2}$ ground state quite closely all along the sequence. The $3p_{3/2}$ level, however, separates rapidly for high Z, tracking the behavior of $3d_{3/2}$. The $3d_{5/2}$ level also begins to separate from the $J=3/2$ levels at around $Z=60$. One should expect this kind of rearrangement to occur quite generally, probably more slowly for $n=4$ levels and more rapidly for those with $n=2$.

The Na sequence is basically a one-electron system. However, this jj clustering of energy levels should also ensue for true multielectron systems. A very simple example is provided by the lowest levels of the boron sequence, where the ground state is $2s^22p$ and the lowest excited states arise from $2s2p^2$. In terms of the relativistic complex, the lowest group of $n=2$ levels should belong to the $(j=1/2)^3$ configurations, with the second group arising from $(1/2)^2(3/2)$. This is shown to be the case in Fig. 2, where we give the scaled excitation energies of the B sequence as determined by a MCDF calculation. The trend towards the asymptote produces a level crossing in the vicinity of $Z=40$, which is not in itself especially unusual. The nonrelativistic theory often predicts a host of level crossings before achieving the asymptotic behavior, depending on the atomic system. What does appear somewhat unusual here is the fact that the lowest level of $2s2p^2$ has come down well below $2s^22p_{3/2}$, which is the upper level of the ground state doublet ^2P. This kind of restructuring of the energy-level spectrum according to the relativistic jj complex is expected to be quite general, with similar shuffling happening for the C sequence, the N sequence, the Al sequence, etc.

One of the more extreme cases is illustrated in Fig. 3, which shows the scaled excitation energies within the $n=3$ complex of the Cl sequence. Near the neutral end of the sequence, the lowest levels are those of the ground-state doublet of $3s^23p^5\,^2P$. However, with increasing Z, relativity rapidly drives the upper $^2P_{1/2}$ level up in the spectrum. The $3s3p^6\,^2S_{1/2}$ level behaves the same way as the $^2P_{1/2}$ level. Meanwhile, a multitude of levels of $3s^23p^43d$, which, however, belong to the relativistic complexes $(1/2)^4(3/2)^3$ and $(1/2)^4(3/2)^2(5/2)$, begins to develop approximately in parallel with the ground state, all of them crossing the rising $^2P_{1/2}$ and $^2S_{1/2}$ levels, which belong to the relativistic complex $(1/2)^3(3/2)^4$. By about $Z=80$ this relativistic restructuring of the spectrum appears to be complete.

Turning now to the relativistic alterations of the asymptotic CI, we take for our first example the simple but classic case of the ground states in the Be isoelectronic sequence. Nonrelativistically, there is a strong mixing of $2p^2$ with $2s^2$, a mixing that persists all along the sequence so that this CI is by far the largest single correlation correction for neutral Be itself. This interaction also gives rise to the well-known linear dependence of the

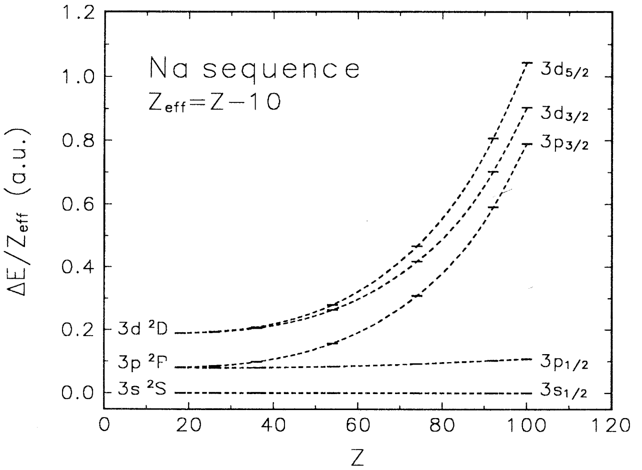

FIG. 1. Scaled Dirac-Fock excitation energies ΔE for the $n=3$ levels of the Na isoelectronic sequence vs the nuclear charge Z.

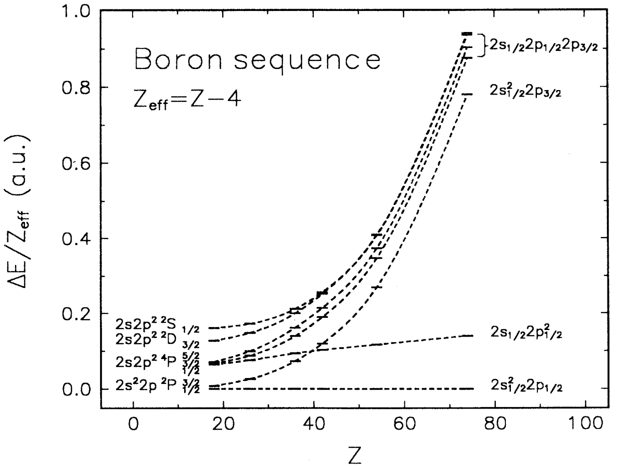

FIG. 2. Scaled MCDF excitation energies ΔE for the $n=2$ complex of the B isoelectronic sequence.

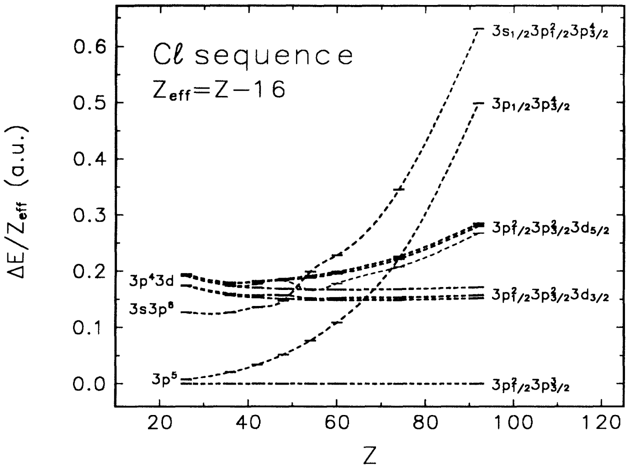

FIG. 3. Scaled MCDF excitation energies ΔE for the lowest $n=3$ complex of the Cl isoelectronic sequence.

correlation energy on Z. For neutral Be the total correlation energy is approximately 0.1 a.u., whereas at $Z=80$ it is more like 1 a.u. In Fig. 4 we show the calculated energy shift produced by this mixing, calculated both nonrelativistically and relativistically. Relativistically, there are actually two $J=0$ terms of $2p^2$: $2p_{1/2}^2$ and $2p_{3/2}^2$.

It is clear that the strong linear dependence of the energy shift has been washed out by relativistic effects. This can be understood by considering the variation of the $2p^2$ mixing coefficients as given in Fig. 5, which shows the transformation from the nonrelativistic to the relativistic complex CI. In Fig. 5 we now plot the CI mixing coefficients vs Z^{-1}, where we also indicate the nonrelativistic infinite Z limit. The lower graph is obtained from the Pauli intermediate coupling mixing of the *LS* configuration-state functions. The upper curve shows exactly the same situation in terms of the relativistic orbitals $2p_{1/2}$ and $2p_{3/2}$ and indicates more clearly the underlying mechanism for the relativistic changes, namely, the disappearance of the $2p_{3/2}^2$ term, which does not belong to the $(1/2)^2$ complex.

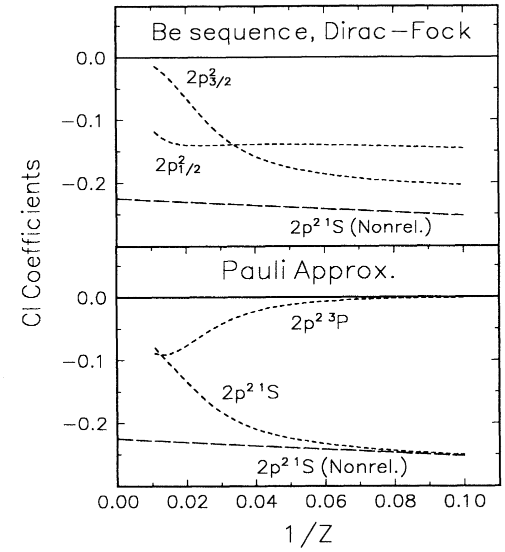

FIG. 5. Mixing coefficients of the $2p^2$ configurations in the ground-state configuration interaction of the Be isoelectronic sequence.

The C sequence provides another, and still more extreme, example of the way relativity alters the asymptotic CI. We consider in particular the ground state $2s^2 2p^2$ with $J=0$. The nonrelativistic complex for this case consists of $2s^2 2p^2\,{}^3P$ and $2p^4\,{}^3P$ and this mixing does produce a linear Z dependence of the energy shift, as indicated in Fig. 6. In this figure, we also show the results of the relativistic CI. The only relativistic configuration-state function corresponding to the lowest energy $J=0$ state is $2s_{1/2}^2 2p_{1/2}^2$. All other relativistic configurations will in-

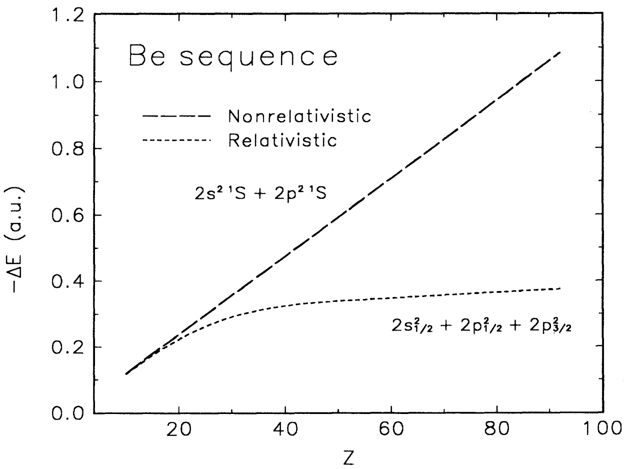

FIG. 4. Ground-state correlation energy shift ΔE arising from the $n=2$ complex configuration interaction in the Be isoelectronic sequence. Nonrelativistic and relativistic CI results are compared.

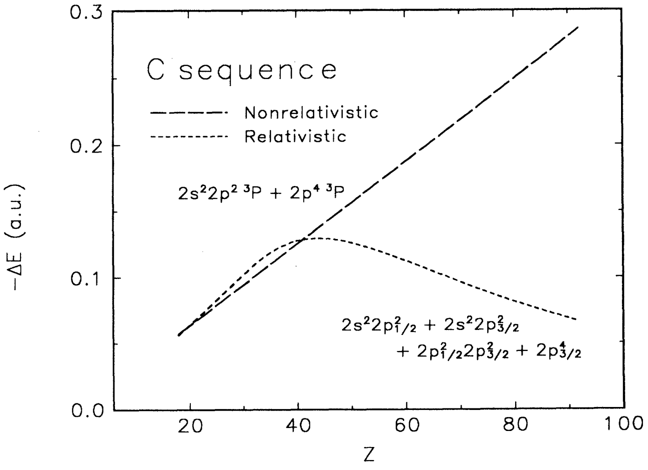

FIG. 6. Ground-state correlation energy shift ΔE arising from the $n=2$ complex configuration interaction in the C isoelectronic sequence. Nonrelativistic and relativistic CI results are compared.

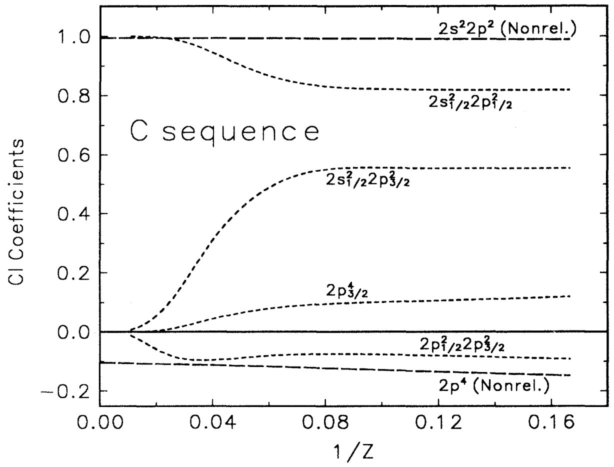

FIG. 7. Nonrelativistic and MCDF configuration mixing coefficients for the lowest $J=0$ state of the C isoelectronic sequence.

volve at least one $2p_{3/2}$, which does not have the same energy in the hydrogenic limit. We therefore find the rather unusual situation where relativity has completely removed the configuration interaction predicted nonrelativistically and the asymptotic state is a pure single configuration. Figure 7 shows the behavior of the mixing coefficients of the pertinent relativistic configurations.

We should remark that this is also true of the lowest $J=1$ and 2 states, the asymptotic configuration being $2s_{1/2}^2 2p_{1/2} 2p_{3/2}$, and it is impossible to construct a $2p^4$ term with which to interact asymptotically. The same situation applies for the B sequence, as well as the analogous Al and Si sequences. No doubt such simplifications will be found to prevail for numerous other cases.

Our final illustrations of this effect are examples in the Mg sequence. The ground state of the Mg sequence is similar to that of Be. However, the two $J=1$ states of the $3s3p$ configuration each provide different examples of the relativistic modifications of charge expansion theory. Nonrelativistically, both the ^3P and the ^1P states will exhibit an asymptotic configuration interaction with $3p3d$.

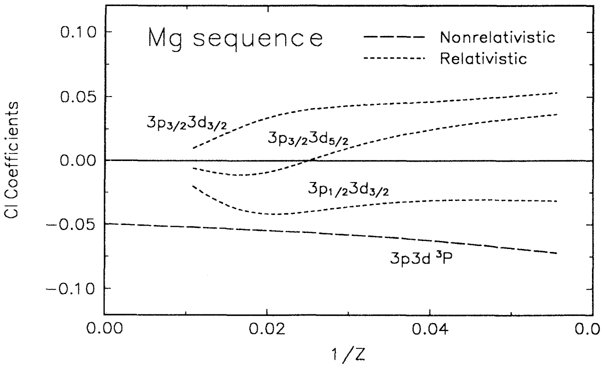

FIG. 8. Comparison of the relativistic and nonrelativistic $3p3d$ mixing coefficients for the lowest $J=1$ (odd) state in the Mg isoelectronic sequence.

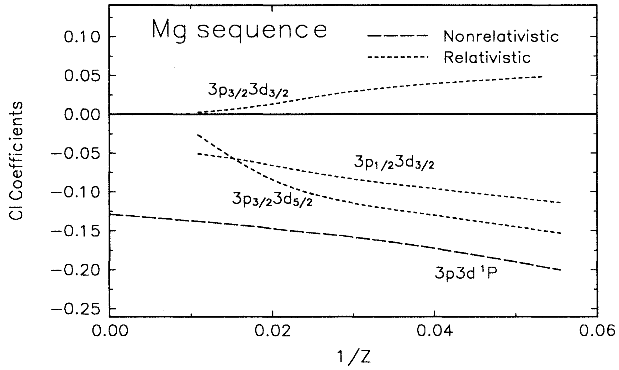

FIG. 9. Comparison of the relativistic and nonrelativistic $3p3d$ mixing coefficients for the second $J=1$ (odd) state in the Mg isoelectronic sequence.

However, relativistically the lowest $J=1$ state arises from $3s_{1/2}3p_{1/2}$, and no $3p3d$ mixing will survive at high Z. Relativity therefore converts this to a single-configuration asymptote. This is illustrated in Fig. 8, where we show the coefficients of the $3p3d$ configurations.

For the second $J=1$ state, however, the relativistically dominant configuration is $3s_{1/2}3p_{3/2}$ and this does have a surviving interaction with $3p_{1/2}3d_{3/2}$, as shown in Fig. 9. The other $3p3d$ configurations, which do not belong to the relativistic complex, are clearly tending toward zero, while this one is not.

V. CONCLUDING REMARKS

Our major conclusions can be summarized by saying that for high Z, in an isoelectronic sequence, one should expect the energy levels to be clustered together according to both their n and their j quantum number occupancy. This is different from a nonrelativistic approach where they cluster according to the principal quantum number alone. Relativity can, and often does, splinter the levels of a nonrelativistic LS-coupled state into different large-Z asymptotes. Thus, for examples, the two levels of the ground configuration doublet of the B or the Al sequence eventually belong to different asymptotic clusters of energy levels.

As in the nonrelativistic theory, the asymptotic level clustering also defines a relativistic complex and therefore also the surviving high-Z configuration interaction. As a consequence, on the whole, the degenerate configuration interaction is substantially reduced over that predicted by the nonrelativistic theory. In many cases the interaction is much weaker, as in the ground states of the Be sequence or the Mg sequence, so that weights of configurations in a relativistic complex are significantly smaller than in their nonrelativistic counterparts. In many other cases, relativistically, the configuration interaction disappears entirely, so that for high Z the ion is correctly described by a single-configuration approximation.

Ultimately, this should simplify the correlation problem for highly charged ions since the proper zeroth-order approximation is represented by either a single configuration or a much more weakly coupled multiconfiguration approximation than indicated by a nonrelativistic theory. This considerably mitigates the need for a multiconfiguration representation of the reference state [18] for a proper treatment of the correlation problem, whether it be a variational multiconfiguration approach or a relativistic many-body perturbation theory (RMBPT). For instance, RMBPT can be applied successfully to high-Z members of the C sequence (see Fig. 5), where the ground state consists of a single (and closed-shell) relativistic configuration $1s^2 2s^2 2p_{1/2}^2$. In contrast, the Be sequence has two degenerate relativistic configurations even at the high-Z limit, $2s^2$ and $2p_{1/2}^2$, thus requiring a multiconfiguration description as the starting point for a perturbation theory. This is probably why Johnson, Sapirstein, and Cheng [19] encountered convergency difficulty for Be-like uranium but not for C-like uranium. Low-Z members of the C sequence, however, require multiconfiguration descriptions because both the $2p_{1/2}^2$ and the $2p_{3/2}^2$ configurations are degenerate in the low-Z limit.

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