PHYSICAL REVIEW A VOLUME 25, NUMBER 2 FEBRUARY 1982

Alkali-metal-atom doublet anomalies and the relation between relativistic and nonrelativistic theories

J. Detrich*
Science Applications Inc., Oak Brook, Illinois 60521

A. W. Weiss
National Bureau of Standards, Washington, D. C. 20234
(Received 14 May 1981)

The single-configuration Dirac-Fock treatment of doublet splittings in alkalilike spectra is examined, and it is shown that the nonrelativistic limit is not the nonrelativistic Hartree-Fock, but a multiconfiguration, core-polarization approximation. The latter is the mechanism which has conventionally been invoked to account for the anomalous doublet splittings of nonpenetrating states in alkalilike atomic systems. Both approaches should thus be capable of representing the doublet anomalies.

The theoretical treatment of excited state doublets of alkalilike atomic systems has been of interest for some time now. The point of interest here concern the inverted, or anomalously narrow, fine structure splitting for nonpenetrating excited states, such as, e.g., the $2p^6nd$ states of sodium or the $3d^{10}4f$ states of copperlike ions. It is clear that the conventional nonrelativistic Hartree-Fock theory cannot account for these anomalous features, since it yields the usual Landé ordering of the levels. The suggestion that this anomaly may be accounted for by core-polarization configuration interaction was first put forward by Phillips,[1] and Lee, Rodgers, Das and Sternheimer[2] have shown that a large part of the effect can be attributed to the anisotropic exchange polarization of non-s core shells. More elaborate treatments have been given by Beck and Odabasi[3] and by Holmgren, Lindgren, Morrison and Martensson.[4]

An alternative approach to this problem is that of the relativistic Dirac-Hartree-Fock (DHF) method. Luc-Koenig[5] has commented extensively on this approach, with and without local exchange approximations, and has shown that the single-configuration DHF method does indeed account for much of the doublet inversion. The classic example of this anomaly has been the $2p^63d$ state of sodium, where the inversion is quite small, of the order of a fraction of a wave number. However, Cheng and Kim[6] have also found that the DHF procedure produces much larger inversions for the $3d^{10}nf$ states of copperlike ions, as large as 40 cm^{-1}. Furthermore, the inversion persists along the isoelectronic sequence as far as Zr^{+11} in general agreement with spectroscopic observations.[7]

At first sight, this might seem somewhat surprising since the single-configuration relativistic treatment apparently does not explicitly include core-polarization effects and thus appears to raise some questions about the mechanism responsible for the doublet anomalies. Luc-Koenig has discussed this question in terms of the different contributions of j-dependent model exchange potentials and relativistic operators and has shown that a relativistic central field model, and therefore implicitly the DHF method, does include the important nonrelativistic core-polarization contribution. In this report we consider this question from a somewhat different viewpoint, namely, that of the structure of the multielectron wave functions.

Our key observation is that $j-j$ coupling, which is required in relativistic treatments, does not translate directly into the LS-coupling scheme of conventional nonrelativistic methods. Assuming different radial functions for the different j components of nl_j orbitals implies an LS-coupling description in terms of a multiconfiguration wave function. This has also been commented on in a recent paper[8] discussing the relation between relativistic and nonrelativistic approximations for the carbon atom, and the point here is that essentially the same observation accounts for the dominant mechanism responsible for these doublet anomalies.

As a concrete example, we will discuss the $2p^6nd$ states; the extension to $3d^{10}nf$ and similar cases should be obvious. A j-j coupled single-configura-

tion wave function has the form,

$$\psi=(2p_{1/2})^2(2p_{3/2})^4 nd_j \ . \tag{1}$$

For our purposes here, we adopt a description of the orbitals in terms of two-component Pauli spinors; the relation between Dirac and Pauli spinors is simple and well understood.[9] As Luc-Koenig has observed, the main contribution to the doublet anomalies arises from large component corrections. The important assumption here is that the orbitals in (1) do not differ greatly from the conventional, nonrelativistic Hartree-Fock.

With this assumption, we can write

$$2p_j=2p+\delta p_j \ . \tag{2}$$

and the multielectron function (1) becomes, to lowest order,

$$\psi=2p^6nd+2\times 2p^5\delta p_{1/2}nd+4\times 2p^5\delta p_{3/2}nd \ , \tag{3}$$

where we have also assumed the Rydberg orbitals nd_j to be well approximated by the nonrelativistic Hartree-Fock nd. This can be written, in terms of some orthonormal set of p functions, as

$$\psi=2p^6nd+\sum_m \lambda_{1m}(2p^5mp\,^1S_0)nd + \sum_m \lambda_{2m}(2p^5mp\,^3P_0)nd \ , \tag{4}$$

the ^1S and ^3P parent terms being the only LS-coupling configurations which can maintain the overall $J=0$ symmetry of the core. Since we have assumed the $2p^6nd$ configuration in (4) to be the nonrelativistic Hartree-Fock function, Brillouin's theorem[10] implies that matrix elements, over the nonrelativistic Hamiltonian and which connect the ^1S coupled terms with this configuration, will vanish. This is not the case for the ^3P coupled terms. It should be noted that, in general, the coefficients in (4) are also dependent on the particular J state even though the radial parts of the nd orbitals are j independent.

At this point, several observations can be made. The nonrelativistic limit of a DHF calculation requires one to compute the wave function (1) in a nonrelativistic approach, and the approximate equivalence of (1) and (4) show that, in general, this limit is not the nonrelativistic Hartree-Fock function. Brillouin's theorem imposes a constraint on the relation between $\delta p_{1/2}$ and $\delta p_{3/2}$, so that the radial dependence of the $2p_j$ orbitals need not be similar to that of the relativistic large components. Nevertheless, the nonrelativistic limit is not the conventional nonrelativistic Hartree-Fock, but a j-dependent version of the unrestricted Hartree-Fock method.

Secondly, the important ^3P coupled terms in (4) are the main core-polarization configurations, which have traditionally been invoked to account for the doublet anomalies in a nonrelativistic treatment. These terms also have a nonvanishing spin-orbit matrix element with the $2p^6nd$ reference state. The above discussion applies to a relativistic treatment, as well as its nonrelativistic limit, if one construes the anaylsis (1)—(4) to apply to the large components or if one takes the orbitals of (1) to be Pauli spinors obtained from a Pauli-like equation. The imposition of different radial j components for the core orbitals in a relativistic calculation is thus equivalent to including core polarization in a nonrelativistic scheme.

We should also note that the ^3P coupled terms in (4) are not pure ^2D symmetry, but also include LS-coupled terms such as $(2p^53p^3P)nd\ ^4P, ^2P, ^4D$, etc. Since these configurations are not coupled electrostatically with the reference configuration, in order to be more fully equivalent to a DHF calculation, the nonrelativistic approach must include intermediate coupling as well as configuration interaction. Finally, we note that the closed-shell case is exempt from these ambiguities. If one removes the nd orbital from the above considerations, the only limiting configuration interaction in (4) is the Brillouin forbidden one, so that, in this case, the nonrelativistic Hartree-Fock is the nonrelativistic limit.

This work was supported in part by the Division of Basic Energy Sciences, Department of Energy.

---

*Present address: NASA Langley Research Center, Hampton, Virginia 23665.

[1]M. Phillips, Phys. Rev. 44, 644 (1933); 45, 428 (1934).
[2]T. Lee, J. E. Rodgers, T. P. Das, and R. M. Sternheimer, Phys. Rev. A 14, 51 (1976).
[3]D. R. Beck and H. Odabasi, Ann. Phys. (N.Y.) 67, 274 (1971).
[4]L. Holmgren, I. Lindgren, J. Morrison, and A. M. Martensson, Z. Phys. A 276, 179 (1976).
[5]E. Luc-Koenig, Phys. Rev. A 13, 2114 (1976); J. Phys. 41, 1273 (1980).
[6]K. T. Cheng and Y. -K. Kim, At. Data Nucl. Data

Tables 22, 547 (1978).
[7]J. Reader and N. Acquista, J. Opt. Soc. Am. 69, 1285 (1979); J. Reader and N. Acquista (private communication); W. C. Martin, in Proceedings of Argonne Workshop on Foundations of Relativistic Theory of Atomic Structure, 1981 (in press).
[8]C. P. Wood and N. C. Pyper, Mol. Phys. 41, 149 (1980).
[9]J. Detrich, Phys. Rev. A 5, 2014 (1972).
[10]L. Brillouin, Actualities Sci. Ind. 71, (1933); C. Møller and M. S. Plesset, Phys. Rev. 46, 618 (1934).