PHYSICAL REVIEW A VOLUME 42, NUMBER 11 1 DECEMBER 1990

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Anomalous doublet splittings of binding energies in Dirac-Fock calculations

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(Received 18 September 1990)

Negative screening parameters for spin doublets have been reported for some atoms by using binding energies from Dirac-Fock calculations. The Dirac-Fock energies for spin doublets fail to converge to the same nonrelativistic limit because of unbalanced treatments of electron-electron correlations and give rise to spurious doublet splittings. We subtract from the Dirac-Fock doublet splittings the corresponding values in the nonrelativistic limit. The corrected doublet splittings form a smooth function of the atomic number and result in positive screening parameters. Detailed analyses are worked out for $3p$ spin doublets as an illustration.

To account for the screening of the nuclear charge on a given orbital electron by other electrons in a many electron atom, Sommerfeld[1] introduced the screening parameters σ_1 and σ_2 in the expanded form of the Dirac eigenenergy and obtained the following expression, in atomic units,

$$E(n,j) = -\frac{1}{2}\left[\frac{(Z-\sigma_1)^2}{n^2}+\frac{\alpha^2(Z-\sigma_2)^4}{n^4}\times\left(\frac{n}{j+1/2}-\frac{3}{4}\right)+\cdots\right]. \quad (1)$$

The first term is the total energy of a nonrelativistic electron, in which σ_1 accounts for the screening effect of other orbitals internal or external to the one under consideration. The second term is due to the combined effect of the mass variation, Darwin term, and spin-orbit interaction. The spin-orbit interaction which gives rise to the spin-doublet splitting is inversely proportional to r^3; for this reason σ_2 accounts dominantly for the screening effect of internal orbitals. Recently Misra, Sah, and Gokhale[2] reported negative screening parameters σ_2 of spin doublets in neutral atoms. The binding energies adopted in the calculation were Dirac-Fock (DF) energies evaluated with Dirac-Fock-Slater (DFS) wave functions;[3] to this approach we refer to as DF(S). Before these authors, Burr and Carson[4] have used the experimental energy values reported by Bearden and Burr[5] in their calculations of σ_2. However, the spin doublets of those atoms with negative σ_2 are unresolved in these experimental data. This negative screening anomaly shows the need to reexamine the formulation used in the study of spin doublets of binding energies.

The theoretical electron binding energy including relaxation is defined as

$$E_b = E_{\text{ion}} - E_{\text{ground}}, \quad (2)$$

where E_{ion} is the total energy of the ion with $N-1$ electrons, and E_{ground} is the total energy of the atom in the ground state. Because the parameter σ_2 is completely determined by the doublet splitting rather than by its absolute position, we concentrate on the splittings of doublet levels. Consider specifically the splitting of $3p$-electron binding energies in neutral atoms of Sc through Zn.

$$\Delta E = E_b[3p_{1/2}] - E_b[3p_{3/2}] = E_{\text{ion}}[3p_{1/2}] - E_{\text{ion}}[3p_{3/2}]. \quad (3)$$

For brevity, we use $[3p_j]$ to denote the configuration with one $3p_j$ electron absent from the ground configuration. Symbolically, we have

$$[3p_{1/2}] = (\text{core}) + 3p_{1/2}3p_{3/2}^4 3d_{3/2}^m 3d_{5/2}^n,$$

and a similar definition for $[3p_{3/2}]$

$$[3p_{3/2}] = (\text{core}) + 3p_{1/2}^2 3p_{3/2}^3 3d_{3/2}^m 3d_{5/2}^n.$$

In the DF formulation,[6,7] the configuration-average energy for an atom or ion is expressed as

$$E_{\text{DF}} = \sum_a N_a I(a) + \sum_a \frac{N_a(N_a-1)}{2}\left[F^0(aa) - \sum_{j\neq 0} C_j(a)F^j(aa)\right] + \sum_{a<b} N_a N_b \left[F^0(ab) - \sum_j D_j(ab)G^j(ab)\right], \quad (4)$$

where $I(a)$ is the one-particle integral including the kinetic energy and nuclear potential energy, N_a is the number of electrons in subshell a, $F^j(aa)$ and $G^j(ab)$ are the

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direct and exchange integrals, respectively, and $C_j(a)$ and $D_j(ab)$ are certain coupling coefficients. Here the summation is over all subshells. In a complete analysis of atomic multiplet structures, one should determine all eigenstates of various total angular momenta and parities. This would involve calculations including nonaverage electrostatic and magnetic effects. Our concern, however, is the splittings of electron binding energies from configurations $[3p_{1/2}]$ and $[3p_{3/2}]$; it is therefore natural to take the configuration average of all the multiplets of each configuration.

The $3p$ doublet splitting in the DF formulation is given by

$$\Delta E_{\mathrm{DF}} = E_{\mathrm{DF}}[3p_{1/2}] - E_{\mathrm{DF}}[3p_{3/2}] . \tag{5}$$

We present ΔE_{DF} and its nonrelativistic limit $\Delta E_{\mathrm{DF-NR}}$ in Table I for neutral atoms of Sc through Zn. Physically the spin-doublet splitting is of relativistic origin and should vanish in the nonrelativistic limit. To explain why $\Delta E_{\mathrm{DF-NR}}$ is nonvanishing in Table I, we consider its major contribution as follows. If we neglect the slight difference in orbital wave functions from the two configurations, we obtain the major contribution of the doublet splitting in the DF formulation as

$$\begin{aligned}\Delta E_{\mathrm{DF}} \approx & -I(3p_{1/2}) + I(3p_{3/2}) - F^0(3p_{1/2}) + 3[F^0(3p_{3/2}) - \tfrac{1}{15} F^2(3p_{3/2})] - 2[F^0(3p_{1/2}3p_{3/2}) - \tfrac{1}{10} G^2(3p_{1/2}3p_{3/2})] \\ & - m[F^0(3p_{1/2}3p_{3/2}) - \tfrac{1}{6} G^1(3p_{1/2}3d_{3/2})] - n[F^0(3p_{1/2}3d_{5/2}) - \tfrac{1}{14} G^3(3p_{1/2}3d_{5/2})] \\ & + m[F^0(3p_{3/2}3d_{3/2}) - \tfrac{1}{60} G^1(3p_{3/2}3d_{3/2}) - \tfrac{9}{140} G^3(3p_{3/2}3d_{3/2})] \\ & + n[F^0(3p_{3/2}3d_{5/2}) - \tfrac{1}{10} G^1(3p_{3/2}3d_{5/2}) - \tfrac{1}{35} G^3(3p_{3/2}3d_{5/2})] . \end{aligned} \tag{6}$$

Furthermore, by taking $3p_{1/2} = 3p_{3/2} = 3p$, $3d_{3/2} = 3d_{5/2} = 3d$, we express the energy expression of the doublet splitting in the nonrelativistic limit approximately by

$$\Delta E_{\mathrm{DF-NR}}^{\mathrm{approx}} = \tfrac{1}{20}(3m - 2n)[G^1(3p3d) - \tfrac{3}{7} G^3(3p3d)] . \tag{7}$$

Unless $G^1(3p3d) - \frac{3}{7} G^3(3p3d)$ is negligibly small, the expression (7) vanishes only for empty $3d$ subshells $m=0$, $n=0$ and for completely filled $3d$ subshells $m=4$, $n=6$. The other case which satisfies the vanishing condition is for $m=2$ and $n=3$, the excited configuration of Mn. In Table I we also present values of $\Delta E_{\mathrm{DF-NR}}^{\mathrm{approx}}$ and compare them with the exact results $\Delta E_{\mathrm{DF-NR}}$ and ΔE_{DF}. From the close agreement between $\Delta E_{\mathrm{DF-NR}}^{\mathrm{approx}}$ and $\Delta E_{\mathrm{DF-NR}}$, we conclude that the anomalous doublet splittings which remain in the nonrelativistic limit come from the nonvanishing energy expression of Eq. (7). When there are unfilled $3d$ subshells, these $3d$ electrons can interact with $3p$ electrons and result in various term structures. The nonrelativistic limits of the energy expressions for $[3p_{1/2}]$ and $[3p_{3/2}]$ are then different linear combinations of these terms; hence, the energy expressions correspond to different nonrelativistic limits. For this reason there arise unbalanced treatments of electron-electron correlations in configurations $[3p_{1/2}]$ and $[3p_{3/2}]$. The anomalous doublet splittings in the nonrelativistic limit should therefore be removed from the relativistic calculations, and the resulting doublet splittings are referred to as those of the corrected Dirac Fock (CDF). On the other hand, for either empty or completely filled $3d$ subshells, the configuration $[3p_{1/2}]$ or $[3p_{3/2}]$ has only one term. The energy expression of the $3p$ doublet splitting vanishes in the nonrelativistic limit, and no spurious contribution exists. In the multiconfiguration Dirac-Fock calculations of B- and F-like ions, Huang *et al.*[8] encountered a similar situation in which the spin-orbit splittings were much larger than experimental data. The spurious nonrelativistic contributions were removed from theoretical spin-orbit splittings before comparisons were made with experiment.

Because the *LS* coupling is more suitable for most atoms with open outer shells, Lindgren and Rosén[9] and Desclaux[10] have taken an average over all relativistic configurations that correspond to a nonrelativistic configuration. These kind of approaches, together with the DFS formulation in which the exchange terms are replaced by a local potential, do not give rise to spurious contributions in the nonrelativistic limits. However, as far as the DF formulation is concerned, the present work pro-

TABLE I. Comparison of $3p$ doublet splittings ΔE_{DF}, their nonrelativistic limits $\Delta E_{\mathrm{DF-NR}}$, and their major contributions $\Delta E_{\mathrm{DF-NR}}^{\mathrm{approx}}$. All energies listed are in atomic units.

Z	m	n	$3m-2n$	$G^1(3p3d)$	$G^3(3p3d)$	$\Delta E_{\mathrm{DF-NR}}^{\mathrm{approx}}$	$\Delta E_{\mathrm{DF-NR}}$	ΔE_{DF}
21	1	0	3	0.4325	0.2619	0.0413	0.0475	0.0659
22	2	0	6	0.4658	0.2826	0.1034	0.1025	0.1261
23	3	0	9	0.4977	0.3022	0.1641	0.1644	0.1942
24	4	1	10	0.4896	0.2948	0.1816	0.1837	0.2196
25	4	1	10	0.5516	0.3352	0.2040	0.2049	0.2508
26	4	2	8	0.5814	0.3534	0.1719	0.1724	0.2284
27	4	3	6	0.6105	0.3716	0.1354	0.1355	0.2029
28	4	4	4	0.6393	0.3893	0.0945	0.0942	0.1747
29	4	6	0	0.6418	0.3888	0.0	−0.0013	0.0923
30	4	6	0	0.6958	0.4242	0.0	−0.0009	0.1110

TABLE II. Comparison of $3p$ doublet splittings from various calculations and from experiment. All energies listed are in atomic units.

Z		DFS[a]	DF(S)[b]	DF[c]	CDF[d]	Experiment[e]
18	Ar	0.007 36	0.006 56	0.006 52	0.006 59	
19	K	0.010 91	0.009 82	0.009 80	0.009 87	
20	Ca	0.015 43	0.014 03	0.014 02	0.014 10	
21	Sc	0.020 10	0.064 50	0.065 90	0.018 40	
22	Ti	0.025 62	0.123 42	0.126 11	0.023 62	
23	V	0.032 14	0.190 22	0.194 22	0.029 86	
24	Cr	0.038 64	0.215 00	0.219 61	0.036 15	
25	Mn	0.048 48	0.246 59	0.250 85	0.045 94	
26	Fe	0.058 60	0.225 12	0.228 38	0.055 95	
27	Co	0.070 19	0.200 66	0.202 91	0.067 41	
28	Ni	0.083 38	0.173 44	0.174 69	0.080 44	0.066
29	Cu	0.096 67	0.093 64	0.092 32	0.093 62	0.081
30	Zn	0.115 18	0.111 76	0.110 96	0.111 86	
31	Ga	0.133 58	0.140 01	0.138 38	0.133 15	0.129
32	Ge	0.161 22	0.174 26	0.173 28	0.157 76	
33	As	0.189 48	0.200 15	0.200 12	0.185 92	
34	Se	0.221 34	0.228 49	0.229 74	0.217 86	
35	Br	0.257 38	0.259 73	0.261 06	0.253 92	
36	Kr	0.297 93	0.294 18	0.293 90	0.294 40	
37	Rb	0.343 46	0.339 51	0.339 32	0.339 80	
38	Sr	0.394 27	0.390 14	0.390 04	0.390 51	0.379

[a]Dirac-Fock-Slater energies using the computer program of Ref. 11.
[b]Dirac-Fock energies evaluated with Dirac-Fock-Slater wave functions.
[c]Dirac-Fock energies using the computer program of Ref. 6.
[d]Dirac-Fock energies corrected for the nonrelativistic limit.
[e]Reference 12.

vides an alternative method to give correct doublet splittings of binding energies.

Various theoretical results of the $3p$ doublet splittings for $Z=18$–38 are compared with experiment in Table II. The doublet splittings of DF(S) and DF are similar and contain spurious contributions because they were both obtained from the same DF energy expressions. The CDF

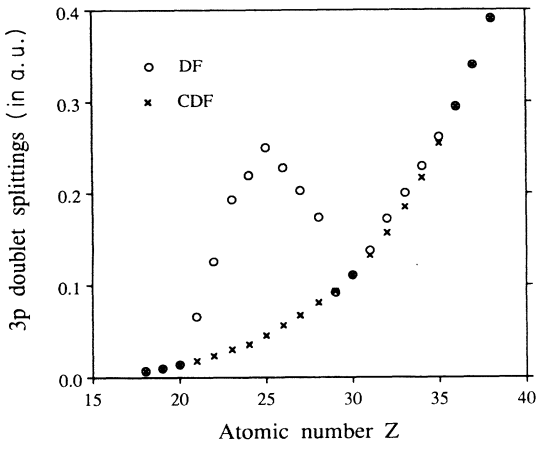

FIG. 1. Comparison of $3p$ doublet splittings of DF and CDF calculations for neutral Ar through Sr.

TABLE III. Sommerfeld screening parameter σ_2 derived from doublet splittings in the Dirac-Fock and in the corrected Dirac-Fock calculations.

Z	σ_2^{DF}	σ_2^{CDF}
18	7.2884	7.2585
19	7.1427	7.1198
20	7.0358	7.0149
21	1.9413	7.1243
22	−0.3900	7.2336
23	−1.9164	7.3459
24	−1.6848	7.5832
25	−1.5424	7.5747
26	0.0661	7.6994
27	1.8137	7.8321
28	3.7301	7.9722
29	8.2753	8.2036
30	8.3138	8.2648
31	8.0935	8.3056
32	7.7819	8.3321
33	7.9039	8.3503
34	8.0330	8.3649
35	8.2008	8.3763
36	8.4066	8.3865
37	8.4113	8.3926
38	8.4134	8.3955

values are close to those of the DFS formulation, which does not suffer from this intrinsic deficiency. Nevertheless, the CDF values are, in principle, better than the DFS values because the exchange effect is treated exactly in the DF formulation. There is reasonable agreement between the CDF and experiment. The $3p$ doublet splittings of DF and CDF are plotted in Fig. 1. There is an apparent anomaly in the DF results for $Z=21-28$, whereas the CDF results form a smooth function of the atomic number Z. The screening parameters σ_2 derived from the DF and CDF values by means of Eq. (1) are presented in Table III. The CDF values also form a smooth function of the atomic number Z, in contrast to the DF values, which show negative screening parameters for $Z=22-25$.

We have elucidated the anomalous doublet splittings of $3p$-electron binding energies in the DF formulation for atoms with partially filled $3d$ subshells. A similar condition exists when there are partially filled $4p$ subshells. However as the overlap of the $4p$ wave function with the $3p$ wave function is small, the exchange integrals in Eq. (7) are expected to be small. This can be seen from Table II and Fig. 1, in which the CDF results deviate only slightly from the DF results for $Z=31-35$, for which the $4p$ subshells are partially filled. Spin doublet splittings for other subshells, such as $3d$, $4p$, $4d$, etc. can be analyzed similarly and are planned to be reported in a separate paper.

This work was supported in part by the National Science Council of the Republic of China.

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