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Relativistic Treatments for Bound-State Atomic Energies*

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The merits of the various methods, used for the determination of relativistic energies, are discussed on the basis of numerical results. It is concluded that, at present, the perturbation approach, based on the Pauli approximation of the Dirac-Breit equation, is more accurate (up to $Z<48$) than the variational approach. Furthermore it is expected that, in any case, the prediction of ionization potentials and energy levels will be equally satisfactory by either method. Consequently, and taking into account the importance of the correlation effects (not only because of the contribution of the correlation energy but also because of their influence on the prediction of the hyperfine structure), it is suggested that it may be worthwhile to direct more efforts towards multiconfigurational Dirac-Breit-Pauli calculations.

Key words: Relativistic bound state atomic energies

Introduction

The ultimate goal of quantum-mechanical calculations is the exact determination of the state energies, including the relativistic corrections and the contributions due to the finite size of the nucleus, and the corresponding state functions. Physical observables are predicted at the same time.

At present, such calculations would be based on the Breit generalization of the Dirac equation. The Dirac-Breit equation constitutes, however, only an approximation and, furthermore, the magnetic and retardation terms of the Breit correction cannot be included in a variational treatment; their contribution must be evaluated, by a perturbation technique, as a first-order correction (Bethe and Salpeter, [3]), although an approximate form of second-order perturbation theory has been used in intermediate-coupling calculations (see the work of Condon and Shortley [4] and the discussion presented by Ermolaev and Jones [5]).

Within the framework of the Hartree-Fock approximation, two approaches exist for the determination of approximate values of the relativistic energies:

1. The Dirac-Breit-Hartree-Fock (v-DBHF) method consists of the determination of the relativistic functions by a Hartree-Fock scheme based on the Dirac-Breit equation, from which the magnetic and retardation terms of the Breit correction have been omitted; their contribution (E_B) should then be evaluated

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using the relativistic functions. (The designation "v" indicates that, except for E_B, the relativistic corrections have been determined by a variational treatment.)

2. The Dirac-Breit-Pauli-Hartree-Fock (p-DBPHF) method involves the determination of the corresponding non-relativistic Hartree-Fock functions, which are then used for the evaluation of the contributions of the relativistic corrections, as given in the Pauli approximation of the Dirac-Breit equation. (The designation "p" indicates that the relativistic corrections have been determined by a perturbation technique.)

In addition, the finite size of the nucleus (as compared with the usual approximation of a point charge with infinite mass) should be taken into account both in the expression of the nuclear potential and in the motion of the nucleus (specific mass effect).

Although much work remains to be done at a lower level of sophistication (especially regarding the evaluation of correlation energies), a trend has been developing in recent years, with more and more efforts directed towards the calculation of relativistic energies by the v-DBHF method. (A wealth of references exists, but they are omitted here as they may be found in the review works of Grant [16] and Ermolaev and Jones [6].) The present work is intended as a justification of the p-DBPHF method.

Results and Discussion

The quantities considered in the present discussion are:

E{v-DBHF(fn)} – relativistic Hartree-Fock energy, evaluated by the v-DBHF method, with the nuclear potential modified in order to take into account the finite size of the nucleus; it does not include the contributions of the magnetic and retardation terms of the Breit correction, the electron-nucleus interactions (other than the electrostatic attraction), or the specific mass effect;

E{v-DBHF(pn)} – same as above, but considering a point nucleus;

E{p-DBPHF(pn)} – relativistic Hartree-Fock energy, evaluated by the p-DBPHF method, considering a point nucleus; it includes the contributions of the magnetic and retardation terms of the Breit correction, all the electron-nucleus interactions, and the specific mass effect;

E_B – magnetic and retardation contributions from the Breit term; in the non-relativistic limit it corresponds to the orbit-orbit and the electron spin-spin contact interactions (Armstrong [1]);

E_{SM} – specific mass effect;

ΔE_R – lowering of the energy, by comparison with the value calculated in the p-DBPHF method, obtained in the variational v-DBHF treatment;

ΔE_N – contribution to the energy, by comparison with the result obtained within the point nucleus approximation, resulting from proper consideration of the finite size of the nucleus in the nuclear potential expression.

The values of E\{v-DBHF(fn)\} and E\{v-DBHF(pn)\} have been taken from the work of Mann and Johnson [18] and Maly and Hussonnois [17], respectively, and the values for E\{p-DBPHF(pn)\}, E_B and E_{SM} are those determined by Fraga and coworkers [8–13] from non-relativistic Hartree-Fock functions.

Table 1 shows the corresponding values for the elements, from He to No, with ground state closed-shell configurations. (In this connection it should be mentioned that v-DBHF calculations have also been carried out for open-shell configurations; however, the corresponding results are not considered here as

Table 1. Total energies (in absolute value) and relativistic corrections (in a.u.)

Element	Z	Total energy			Corrections		
		E{v-DBHF(fn)} [18]	E{v-DBHF(pn)} [17]	E{p-DBPHF(pn)} [8–13]	ΔE_R	$E_B + E_{SM}$ [8–13]	ΔE_N
He	2	2.8618	2.8618	2.8617	0.0	0.0001	0.0
Be	4	14.5759	14.5759	14.5752	0.0	0.0007	0.0
Ne	10	128.6919	128.6920	128.6751	0.0007	0.0162	0.0001
Mg	12		199.9353	199.9024	0.0017	0.0312	
A	18	528.6837	528.6854	528.5356	0.0194	0.1304	0.0017
Ca	20		679.7128	679.4916	0.0328	0.1884	
Zn	30	1794.6122	1794.6277	1793.4731	0.4144	0.7402	0.0155
Kr	36	2788.8597	2788.8961	2786.2073	1.3159	1.3729	0.0364
Sr	38		3178.1267	3174.9710	1.4771	1.6786	
Cd	48	5593.3191	5593.4802	5582.8536	6.9198	3.7068	0.1611
Xe	54	7446.8985	7447.2186	7426.7089	14.9856	5.5241	0.3201
Ba	56		8136.0530	8110.7773	19.0291	6.2466	
Yb	70	14067.7301	14069.3615	13973.565	82.6843	13.1122	1.6314
Hg	80	19649.0836	19653.870	19430.911	202.4843	20.4747	4.7864
Rn	86	23602.4542	23611.517	23253.331	332.1107	26.0753	9.0628
Ra	88		25039.773	24622.183	389.4318	28.1582	
No	102	36743.3761	36793.382	35629.187	1118.2363	45.9587	50.0059

they were obtained using the formulation developed by Grant [14, 15] for closed shells.) In this Table the values of ΔE_R and ΔE_N have been approximated, respectively, by

$$\Delta E_R = E\{\text{p-DBPHF(pn)}\} - [E_B + E_{SM}] - E\{\text{v-DBHF(pn)}\},$$

$$\Delta E_N = E\{\text{v-DBHF(fn)}\} - E\{\text{v-DBHF(pn)}\}.$$

The values of ΔE_R, ΔE_N, and $(E_B + E_{SM})$ may be used for a discussion of the accuracy of the perturbational and variational methods. Inspection of Table 1 shows that, for $Z < 102$, it is $\Delta E_N \ll E_B + E_{SM}$, which indicates that there is no justification in considering the effect of the finite size of the nucleus if the contribution of the Breit term is not included. The values of ΔE_R and ΔE_N can be used to estimate the order of magnitude of the relativistic correction neglected in the DBPHF(pn) method; on the other hand, $(E_B + E_{SM})$ plays the same role for the DBHF method. As seen, up to $Z \simeq 48$, $(\Delta E_R + \Delta E_N) < (E_B + E_{SM})$; that is, the error in $E\{\text{v-DBHF(pn)}\}$ and $E\{\text{v-DBHF(fn)}\}$ is larger than the error in $E\{\text{p-DBPHF(pn)}\}$.

Therefore it must be concluded that the perturbation approach gives better results for light atoms (up to $Z \simeq 48$) than the variational treatments, as carried out until the present.

In addition it must be remembered that the neglect of correlation affects both types of treatments. In this connection two points must be mentioned. First of all it is known that for $Z < 14$ the correlation energy is greater than the relativistic corrections; the importance of its consideration is evident from Table 2. On the other hand it is also known (Armstrong [2] and Fraga and Malli [7]) that correlation is extremely important in hyperfine structure calculations.

The prediction, within the p-DBPHF method, of ionization potentials (Fraga, Saxena, and Karwowski [12]) and transitions (except when inner core electrons are involved) should be comparable to that obtained by the other methods. This assumption is based on the fact that past experience (Fraga and coworkers [8–13]) has shown E_B to be essentially independent of ionization or excitation (under the restriction mentioned above) and it is expected that ΔE_R and ΔE_N will behave similarly.

It seems, therefore, that perhaps more efforts should be directed towards multiconfigurational Dirac-Breit-Pauli calculations, in an effort to include ΔE_C and $(E_B + E_{SM})$ rather than ΔE_R.

Table 2. Correlation energies, ΔE_C (in a.u.), for various atoms

Element	Z	Total energy		ΔE_C	$E_B + E_{SM}$	ΔE_R	ΔE_N
		Experimental [19]	Theoretical[a]				
He	2	2.9034	2.8617	0.0417	0.0001	0.0	0.0
Be	4	14.6685	14.5752	0.0933	0.0007	0.0	0.0
Ne	10	129.0502	128.6757	0.3745	0.0162	0.0007	0.0001
A	18	529.1121	528.5533	0.5588	0.1304	0.0194	0.0017

[a] Approximated from the values of Mann and Johnson [18] by correction with $(E_B + E_{SM})$.

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