

AN APPLICATION OF RELATIVISTIC PSEUDOPOTENTIALS IN ATOMIC HARTREE-FOCK CALCULATIONS: LITHIUM SERIES*

BY J. KARWOWSKI

Institute of Physics, Nicholas Copernicus University, Toruń**

AND M. SZULKIN

Division of Theoretical Physics, Teachers College, Częstochowa***

(Received December 12, 1978)

Two kinds of radial corrections have been added to the Hartree-Fock spherical potential in order to take into account relativistic effects. Excitation energies and transition probabilities were calculated and compared with the results of fully relativistic Dirac-Hartree-Fock and non-relativistic Hartree-Fock calculations for a number of three-electron atoms. The results indicate that the corrections allow us to include a major part of relativistic effects within a simple, non-relativistic computational scheme.

1. Introduction

The most rigorous way of taking into account relativistic effects is the Dirac-Hartree-Fock (DHF) method with perturbational inclusion of the Breit term [1, 2]. Although a computer program for this method is generally available [2] and extensively used (see e.g. [3, 4]), the calculations are much more complicated and expensive than in the non-relativistic case. Recently some work was done on the problem of introducing effective potentials to the non-relativistic Hartree-Fock (HF) equations in order to incorporate in this way the major part of relativistic effects within a non-relativistic approach [5, 6]. In the approach by Cowan and Griffin [5] the potential consisting of the mass-velocity and Darwin terms of the Pauli equation has been added to the HF spherical potential. In spite of completely neglecting the spin-orbit interaction a dramatic improvement in the results was obtained compared to pure HF calculations. In this paper the complete Pauli correction, including the spin-orbit term, was used instead. This modification of the

* Sponsored by the Polish Academy of Sciences, project No. MR. I. 5.

** Address: Instytut Fizyki, Uniwersytet M. Kopernika, Grudziądzka 5, 87-100 Toruń, Poland.

*** Address: Pracownia Fizyki Teoretycznej, Wyższa Szkoła Pedagogiczna, A. Zawadzkiego 13/15, 42-201 Częstochowa, Poland.

HF method is referred to as HFRC. Another approach was proposed by Karwowski and Kłobukowski [6], who derived a relativistic pseudopotential from requirements imposed upon asymptotic behaviour of the solutions of the radial equation. The pseudopotential, which includes also spin-orbit effects, may be introduced in any program solving a radial Schrödinger equation. In the present paper it was applied in atomic HF calculations¹. We shall refer hereafter to this kind of modification of the HF method as the HFRA method. The pilot calculations reported here were performed for several members of the lithium isoelectronic series.

2. Method

The calculations were performed using the numerical Hartree-Fock program developed by Froese-Fischer [8] with relativistic correction terms added to the spherical one-electron HF potential. Two types of the correction terms were used²:

HFRA method. The pseudopotential derived from requirements imposed upon asymptotic behaviour of the radial functions has the form [6]:

$$W_A(r, E) = \alpha^2[(E - V(r))^2 - V(r)^2/2k], \quad (1)$$

where $\alpha \approx 1/137$ is the fine structure constant, E is the orbital energy of the electron and $V(r)$ is the one-electron Hartree-Slater central field potential with local exchange function. The potential $V(r)$ used in this paper is the same as that proposed by Cowan [9]. The quantum number $k = \varepsilon(j+1/2)$, where $\varepsilon = \pm 1$ and $j = l + \varepsilon/2$ (j is the total and l — orbital angular momentum quantum number).

HFRC method. The pseudopotential consists of the radial parts of the mass-velocity, Darwin and spin-orbit terms of the Pauli equation

$$W_C(r, E) = \alpha^2 \left[(E - V)^2 + \frac{1}{2r} \frac{dV}{dr} \left[\delta_{kl} \left(\frac{r}{R} \frac{dR}{dr} - 1 \right) + k - 1 \right] \right] / [1 + \alpha^2(E - V)/2], \quad (2)$$

where R is the radial function and δ_{kl} — the Kronecker delta. Due to the factor $1/(1 + \alpha^2(E - V)/2)$, the singularity of the Darwin and spin-orbit terms for $r \rightarrow 0$ is r^{-2} rather than r^{-3} [5].

The local approximation of the exchange function has been employed only in the relativistic pseudopotentials. In the non-relativistic part of the self consistent field (SCF) equations the rigorous HF exchange was used. The SCF equations were solved using the routine iterative method. Since the SCF potential depends, in an explicit way, on the eigenvalue E being different for different orbitals, the solutions, in general, are not orthogonal. The nonorthogonality is however negligible in all the cases under consideration (the overlap integral is always less than 0.001).

¹ Very recently the same pseudopotential has also been used in molecular SCF X α Scattered Wave calculations [7].

² All quantities are expressed in atomic units.

Transition probabilities have been characterized by the oscillator strengths calculated using the standard formula:

$$f(nlj, n'l'j') = \frac{2}{3} \Delta E \frac{2j'+1}{2j+1} \left\{ \begin{matrix} l & j & 1/2 \\ j' & l' & 1 \end{matrix} \right\}^2 |\langle nl \| \mathbf{D} \| n'l' \rangle|^2, \quad (3)$$

where $nlj, n'l'j'$ are quantum numbers describing the initial and the final states, respectively, ΔE is the transition energy and \mathbf{D} is the transition operator.

3. Results

The energies of $2s_{1/2} \rightarrow 2p_{1/2}$, $2s_{1/2} \rightarrow 2p_{3/2}$, $2s_{1/2} \rightarrow 3p_{1/2}$, $2s_{1/2} \rightarrow 3p_{3/2}$ transitions and the corresponding oscillator strengths (for length and velocity transition operators) were calculated for a number of atoms belonging to the lithium isoelectronic series. Both ground and excited states of each atom were obtained allowing all orbitals to be varied (no frozen core). In the evaluation of the oscillator strengths calculated rather than experimental values of ΔE were used. The results of HFRA and HFRC calculations are given in Table I (transition energies) and Table II (oscillator strengths). For comparison, the results of HF and DHF calculations [3] are also given.

Transition energies, fine structure splittings and transition probabilities obtained by means of the pseudopotentials agree very well with the DHF results. For the transition energies the maximum error calculated relative to DHF ($2s \rightarrow 2p$ transition of Ar XVI) decreases from 12% (HF) to 2.3% (HFRA) and 1.7% (HFRC). The remaining error is of the same order of magnitude as the contribution of the Breit correction.

TABLE I

Energies (in a.u.) of $2s \rightarrow 2p$ and $2s \rightarrow 3p$ transitions

	$2s \longrightarrow 2p^a$				$2s \longrightarrow 3p^a$			
	HF ^b	HFRA	HFRC	DHF ^b	HF ^b	HFRA	HFRC	DHF ^b
LiI	0.0677	{0.0677 0.0677}	{0.0677 0.0677}	{0.0677 0.0677}	0.140	{0.140 0.140}	{0.140 0.140}	{0.140 0.140}
CIV	0.296	{0.297 0.298}	{0.296 0.297}	{0.297 0.297}	1.46	{1.46 1.46}	{1.46 1.46}	{1.46 1.46}
OVI	0.441	{0.444 0.446}	{0.442 0.445}	{0.443 0.445}	3.03	{3.04 3.04}	{3.03 3.03}	{3.03 3.03}
NeVIII	0.585	{0.591 0.599}	{0.586 0.595}	{0.589 0.596}	5.16	{5.18 5.18}	{5.17 5.17}	{5.17 5.17}
ArXVI	1.15	{1.21 1.33}	{1.16 1.29}	{1.18 1.30}	19.2	{19.4 19.5}	{19.3 19.4}	{19.4 19.4}

^a For HFRA, HFRC and DHF methods the first doublet component corresponds to $s_{1/2} \rightarrow p_{1/2}$ transition and the second one to $s_{1/2} \rightarrow p_{3/2}$. ^b From [3].

TABLE II

Oscillator strengths ($\times 10^3$) for $2s \rightarrow 2p$ and $2s \rightarrow 3p$ transitions

	$2s \longrightarrow 2p^a$				$2s \longrightarrow 3p^a$			
	HF ^b	HFRA	HFRC	DHF ^b	HF ^b	HFRA	HFRC	DHF ^b
length								
LiI	255	255	255	255	1	1	1	1
	510	511	510	511	2	2	2	2
CIV	97	97	97	97	66	66	66	66
	195	195	195	195	133	132	133	132
OVI	67	67	67	67	87	87	87	87
	134	136	135	135	175	174	174	174
NeVIII	51	51	51	51	100	99	100	99
	102	104	104	104	199	198	198	198
ArXVI	26	27	26	26	121	120	121	120
	52	60	58	58	241	236	237	236
velocity								
LiI	262	264	264	264	1	1	1	1
	523	529	529	529	2	2	2	2
CIV	104	108	107	107	65	64	64	64
	208	215	215	215	120	128	129	128
OVI	72	76	75	75	86	85	86	85
	144	152	151	151	172	170	171	170
NeVIII	55	59	58	58	98	98	98	98
	109	118	117	117	197	194	195	195
ArXVI	27	34	29	30	120	118	120	119
	54	69	65	66	240	233	235	234

^a In each case the first number corresponds to $s_{1/2} \rightarrow p_{1/2}$ transition and the second one to $s_{1/2} \rightarrow p_{3/2}$.^b From [3].

REFERENCES

- [1] I. P. Grant, *Adv. Phys.* **19**, 747 (1970).
- [2] J. P. Desclaux, *Comput. Phys. Commun.* **9**, 31 (1975).
- [3] L. Armstrong, W. R. Fielder, D. L. Lin, *Phys. Rev.* **A14**, 1114 (1976).
- [4] J. P. Desclaux, D. F. Mayers, F. O'Brien, *J. Phys.* **B4**, 631 (1971).
- [5] R. D. Cowan, D. C. Griffin, *J. Opt. Soc. Am.* **66**, 1010 (1976).
- [6] J. Karwowski, M. Kłobukowski, *Acta Phys. Pol.* **A54**, 237 (1978).
- [7] M. Kłobukowski, Thesis, Nicholas Copernicus University, Toruń 1978.
- [8] C. Froese-Fischer, *Comput. Phys. Commun.* **4**, 107 (1972).
- [9] R. Cowan, *Phys. Rev.* **163**, 54 (1967).