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THE EFFECT OF CORE POLARIZATION ON OSCILLATOR STRENGTHS AND ON THE LOCATIONS OF ENERGY LEVELS IN SODIUM*

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The effect of core polarization on the oscillator strengths and on the energies of $3s \rightarrow np$ ($n = 3, 4, 5, 6$) transitions in sodium atoms is investigated. The polarization correction is included by adding an effective term with one adjustable parameter to the Hartree-Fock core potential in the SCF equation for the outer electron. As a result an essential improvement in the agreement between calculated and observed quantities is obtained.

1. *Introduction*

The simplest way to determine the wavefunction of the valence electron of an alkali atom is to use an effective empirical potential to describe the closed shell core. An excellent review of different ways of dealing with the problem was recently given by Bardsley [1]. An alternative approach is based on the HF (Hartree-Fock) approximation. The HF core potential may be determined in a single SCF (Self Consistent Field) calculation for a selected state (say for the ground state) and then kept fixed for all the other states. Since the numerical HF programme developed by Froese-Fischer [2] is easily available, this scheme became a rather standard routine. This kind of treatment neglects the correlation effects. One of these effects, known as polarization of the core by the outer electron, may be treated in a relatively simple way. The first quantum mechanical description of core polarization was given by van Vleck and Whitelaw [3]. Then several authors investigated

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the influence of this effect on the location of the energy levels (e.g. [4, 5]) and on the transition probabilities (e.g. [6–11]). The core polarization was taken into account either by a modification of the transition moment integral [6–10] or within a perturbational scheme [11]. The perturbational calculation by Garpman [11] most accurately predicts the oscillator strengths for sodium atom.

In the present paper we investigate the core polarization effect on both the transition probabilities and the excitation energies of sodium. We assume that the valence electron moves in the field of a polarized HF frozen core. The core polarization effect is introduced by adding to the HF core potential an effective polarization term.

2. *Method*

In the adiabatic approximation the wavefunction for an alkali atom may be written in the form[1]

$$\Psi_n(R, r) = \chi(R; r)\psi_n(r), \tag{1}$$

where R denotes the coordinates of all core electrons, r — the coordinates of the valence electron, and n is to distinguish different states. The wavefunction for the core electrons $\chi(R; r)$ depends on r only parametrically. It is the lowest energy eigenfunction of the Schrödinger equation

$$[H_c(R)+V(R, r)]\chi(R; r) = U(r)\chi(R; r), \tag{2}$$

where $H_c(R)$ is the core Hamiltonian and $V(R, r)$ is the Coulomb interaction between the core electrons and the valence electron. The eigenvalue equation for ψ_n is

$$[H_1(r)+U(r)]\psi_n(r) = E_n\psi_n(r), \tag{3}$$

where $H_1(r)$ is the one-electron Hamiltonian consisting of the kinetic energy and the nuclear attraction terms. If we replace $V(R, r)$ by an average taken over the valence electron distribution in a given state, then Eq. (2) becomes

$$[H_c(R)+\overline{V}_n(R)]\chi^0(R) = \overline{U}^0\chi^0(R), \tag{4}$$

where $\overline{V}_n(R) = \langle\psi_n(r)|V(R, r)|\psi_n(r)\rangle_r$ and $\langle\ \rangle_r$ means integration over r. The potential energy $U(r)$ in Eq. (3) is then replaced by

$$U^0(r) = \langle\chi^0(R)|H_c(R)+V(R, r)|\chi^0(R)\rangle_R. \tag{5}$$

In particular, if (4) is solved using the HF method, then $U^0(r)$ is the HF core potential. One of the main factors neglected in the case of the HF treatment is the effect of the core polarization by the valence electron. In order to take it into account we express $\chi(R; r)$ in the form

$$\chi(R; r) = \chi^0(R)+\chi^1(R; r), \tag{6}$$

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[1] For simplicity we neglect here the exchange between the core electrons and the valence electron. However, in all calculations we take it into account.

where $\chi^1(R;r)$ is a correction orthogonal to $\chi^0(R)$ resulting from the perturbation $W(R,r) = V(R,r)-\overline{V}_n(R)$. After substituting expansion (6) into Eq. (2), multiplying the equation by $\chi^0(R)$ and integrating over R we obtain

$$U(r) = U^0(r)+\overline{W}(r), \tag{7}$$

where

$$\overline{W}(r) = \langle\chi^0(R)|W(R,r)\,|\chi^1(R;r)\rangle_R. \tag{8}$$

The asymptotic form (for large r) of the correction term is [13]

$$\overline{W}(r) \sim -\alpha/2r^4, \tag{9}$$

where α is the dipole polarizability of the core. Hence, a simple correction due to the core polarization may be introduced by adding to the HF core potential, in the equation determining ψ_n, a term which behaves asymptotically like $\overline{W}(r)$.

In the present paper we used, for all the considered states of an atom, that core potential, determined by the HF calculation for the ground state of the atom with the correction term

$$W_d(r) = -\alpha/2(r^2+d^2)^2, \tag{10}$$

where d is an empirical parameter and α — the experimental value of the dipole polarizability of the core.

3. *Results*

The calculations have been performed for $3s \to np$ ($n = 3, 4, 5, 6$) transitions in sodium atoms using the Froese-Fischer atomic HF programme [2] modified by Baylis [14] and by one of the authors (M.S.) in order to include the core polarization effect. The value of the dipole polarizability of the core, $\alpha = 0.945$ a.u., has been taken from [1]. The parameter $d = 1.01$ a.u. has been chosen to reproduce the experimental value of the $3s \to 3p$ transition energy.

The values of the transition energies and of the multiplet splitting, calculated with and without the core polarization correction, are given in Table I. The percentage error

$$\delta = \frac{|E^{\mathrm{exp}}-E^{\mathrm{calc}}|}{E^{\mathrm{exp}}}\,100\,\%, \tag{11}$$

where superscripts "exp" and "calc" refer to the experimental and calculated quantities respectively, is also given there. As seen, for the transition energies the values of δ are reduced from 4%—6% for HF calculations to 0.0%—0.7% when $W_d(r)$ correction is included. The corresponding figures for the fine structure splitting are, respectively, 28%—33% and 5%—10%.

The values of the oscillator strengths calculated for the dipole (f_l) and for the velocity (f_v) operators are given in Table II. As a measure of the quality of the wavefunctions the

TABLE I

Transition energies from the ground state of sodium and fine structure splitting of the upper states (in cm^{-1}) calculated without (HF) and with (HFP) core polarization correction[a]

Upper state	Transition energies			Fine structure splitting		
	HF	HFP	Exp.[b]	HF	HFP	Exp.[b]
$3p$	15913 (6.2%)	16963 (0.0%)	16968	11.476 (33%)	16.086 (6%)	17.196
$4p$	28889 (4.6%)	30454 (0.6%)	30271	3.807 (32%)	5.147 (9%)	5.63
$5p$	33584 (4.2%)	35274 (0.7%)	35042	1.697 (33%)	2.262 (10%)	2.52
$6p$	35812 (4.0%)	37548 (0.7%)	37297	0.897 (28%)	1.187 (5%)	1.25

[a] Values of the relative error δ are given in parentheses.

[b] Experimental values taken from [15].

TABLE II

Oscillator strengths f_l and f_v (multiplied by 10^3), and their relative differences p, for the transitions from the ground state of sodium[a]

Upper state		HF	HFP	GP	Exp.
$3p$	f_l	1052.	975.6	1031.	975.
	f_v	908.8	974.6	902.8	
	p	14.7%	0.1%	13.3%	
$4p$	f_l	13.60	12.49	11.67	14.2
	f_v	11.42	12.63	10.57	
	p	17.5%	1.1%	9.9%	
$5p$	f_l	1.989	1.793	1.526	2.21
	f_v	1.600	1.814	1.381	
	p	21.8%	1.2%	10.0%	
$6p$	f_l	0.5998	0.5317	0.4180	0.73
	f_v	0.4660	0.5382	0.3801	
	p	25.3%	1.2%	9.5%	

[a] The values have been calculated using the wavefunctions obtained without (HF) and with (HFP) core polarization correction. For comparison the experimental [16] (Exp) values and those obtained by Garpman [15] (GP) are given.

relative differences

$$p = \frac{|f_l - f_v|}{\sqrt{f_l f_v}}\, 100\% \tag{12}$$

between f_l and f_v are also given. The influence of the core polarization is significant.

As one could expect, the inclusion of the $W_d(r)$ correction does not improve the values of the transition probabilities f_a calculated using the acceleration operator. In all the considered cases $f_a/f_l \sim 10^3$, that includes the pure HF calculation as well as after taking the polarization effect into account. Since f_a is most sensitive to the quality of the wavefunction near the origin, formula (10), based on the asymptotic behaviour of the polarization potential, cannot be adequate in this case.

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