Calculations on polarization properties of alkali metal atoms using Dirac–Fock plus core polarization method*

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A semi-empirical atomic structure model method is developed in the framework of a relativistic case. This method starts from Dirac–Fock calculations using B-spline basis set. The core-valence electron correction is then treated in a semi-empirical core polarization potential. As an application, the polarization properties of alkali metal atoms, including the static polarizabilities and long-range two-body dispersion coefficients, have been calculated. Our results are in good agreement with the results obtained from *ab initio* relativistic many-body perturbation method and the available experimental measurements.

Keywords: Dirac–Fock, core polarization, polarizabilities, alkali metal atoms

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1. Introduction

The polarizability of an atom can be considered as a measure of the response of the charge cloud to an external electric field. Studies of polarizabilities of neutral atoms and ions have been of great interest in many different physical applications.[1–12] In the optical clock cases, the knowledge of static polarizabilities of clock states is used to evaluate the blackbody radiation (BBR) shift, which is one of the main sources of systematic errors.[1,2] Dynamic polarizabilities can be used to identify the magic wave lengths of transition states[3,4] and tune-out wave lengths of atomic states at which polarizability-related quantities are equal to zero.[11,12] The identification of magic wavelengths and their use in making optical lattices have resulted in the development of optical lattice clocks.[3,4] On the other hand, the calculations of imaginary frequency dynamic polarizabilities can be used to construct the long-range dispersion potential, which plays an important role in Bose–Einstein condensates, ultracold collision experiments, and ultracold photoassociation spectroscopies.[8–10] For example, since the elastic collisions are sensitive to the long-range potential, the knowledge of the van der Waals dispersion coefficients influences the predictions of the signs and magnitudes of scatting lengths, which determine the stability and structure of Bose–Einstein condensates.[9]

The experimental techniques that are used to measure atomic and ionic polarizabilities mainly include E–H balance method,[13] the deflection of atomic beam by electric field,[14] the atom interferometry,[15–17] cold atom velocity change,[18] and so on. However, precise measurement of polarizabilities is quite challenging. The experimental values of polarizabilities of many heavy elements are still not available, especially for excited states. Therefore, accurate theoretical studies of atomic and ionic polarizabilities are of particular interest.

There have been a number of theoretical methods applied to the calculations of atomic and ionic polarizabilities for many-electron atomic systems,[19] including relativistic all-order and coupled cluster (RCC) method,[20,21] relativistic many-body perturbation theory (RMBPT) method,[22,23] and model potential methods.[24–28] It is known that *ab initio* all-order, RCC, and RMBPT methods are more sophisticated and require larger computational resources, although they can be applied to high-precision calculations. The model potential method is an economic and practical method, which has the advantage in reducing the size of the calculation. Among different forms of model potentials, the semi-empirical core polarization potential is mostly adopted. For the light atomic system, the configuration interaction calculations with a semi-empirical core potential (CICP)[24] can give almost the same precision results as the RCC and RMBPT methods. Although a relativistic CICP method has been applied to Zn, Cd, and Hg,[26,27] most implementations of CICP method are based on non-relativistic Hartree–Fock calculations, which cannot be applied to predict the properties of spin-orbital doublet in a natural way and cannot work in heavy atomic systems well.

For these motivations, we developed a relativistic core polarization potential method and applied it to calculate the

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polarization properties of alkali metal atoms, including the static multipolar polarizabilities and long range dispersion coefficients. This paper is organized as follows. An introduction of the theoretical method will be given in the second section. The static polarizabilities of the ground and first seven excited states for neutral alkali metal atoms are presented and compared with results obtained from other theoretical methods and experimental measurements in the third section. Finally, a summary is given in the fourth section. Atomic units are used in this work.

2. Methodology

2.1. Dirac–Fock calculaitons based on B-spline basis set

The basic idea of the theoretical method in this work is that an atom or ion system is simplified as a frozen core part and a valence electron part. The first step is the Dirac–Fock (DF) calculation of frozen core part to obtain the core orbital functions. The DF calculation begins with the equation

$$\left(\sum_i H_{\rm D}(\boldsymbol{r}_i)+\sum_{i<j}\frac{1}{r_{ij}}\right)\psi(\boldsymbol{r})=E\psi(\boldsymbol{r}), \tag{1}$$

where $H_{\rm D}$ is the single-electron Dirac Hamiltonian

$$H_{\rm D}(\boldsymbol{r}_i)=c\boldsymbol{\alpha}\cdot\boldsymbol{p}+c^2(\boldsymbol{\beta}-1)+V(\boldsymbol{r}_i). \tag{2}$$

Here, c is the speed of light, $\boldsymbol{p}$ is the momentum operator, and, $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are the Dirac matrices. The Dirac wave function, $\psi(\boldsymbol{r})$, can be written as

$$\psi(\boldsymbol{r})=\frac{1}{r}\begin{pmatrix}P_{n\kappa}(r)\Omega_{\kappa m}(\hat{r})\\ {\rm i}Q_{n\kappa}(r)\Omega_{-\kappa m}(\hat{r})\end{pmatrix}, \tag{3}$$

where the radial wave function $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small components, respectively, $\Omega_{\kappa m}(\hat{r})$ and $\Omega_{-\kappa m}(\hat{r})$ correspond to the angular components. The quantum number κ is connected with j and ℓ:

$$\kappa=\ell(\ell+1)-j(j+1)-\frac{1}{4}. \tag{4}$$

In the present work, the large and small components of Dirac wave functions are expanded in terms of an N-dimensional B-spline basis of k order,

$$P_{n\kappa}(r)=\sum_{i=1}^{N}C_i^{P,n}B_{i,k}(r), \tag{5}$$

$$Q_{n\kappa}(r)=\sum_{i=1}^{N}C_i^{Q,n}B_{i,k}(r). \tag{6}$$

The B-splines are defined on the finite cavity $[0,R_{\rm max}]$, which is set as a knot sequence, $\{t_i\}$, satisfying an exponential distribution.[29–31] More details of B-splines are described in Ref. [32]. Combining the variational principle with the relativistic wave function boundary condition,[33] a $2N\times 2N$ symmetric generalized eigenvalue equation can be obtained

$$\boldsymbol{A}\upsilon=\varepsilon\boldsymbol{B}\upsilon. \tag{7}$$

The Hamiltonian matrix $\boldsymbol{A}$ is

$$\boldsymbol{A}=\begin{pmatrix}\boldsymbol{V}^{PP}+\boldsymbol{V}_{\rm d}^{PP}-\boldsymbol{V}_{\rm ex}^{PP} & \boldsymbol{\Pi}^{PQ}-\boldsymbol{V}_{\rm ex}^{PQ}\\ \boldsymbol{\Pi}^{QP}-\boldsymbol{V}_{\rm ex}^{QP} & \boldsymbol{V}^{QQ}-2c^2\mathbf{S}^{QQ}+\boldsymbol{V}_{\rm d}^{QQ}-\boldsymbol{V}_{\rm ex}^{QQ}\end{pmatrix}+A'. \tag{8}$$

The overlap matrix $\boldsymbol{B}$ is

$$\boldsymbol{B}=\begin{pmatrix}\mathbf{S}^{PP} & 0\\ 0 & \mathbf{S}^{QQ}\end{pmatrix}. \tag{9}$$

where $\boldsymbol{V}^{PP}$, $\boldsymbol{V}^{QQ}$, $\boldsymbol{V}_{\rm d}^{PP}$, $\boldsymbol{V}_{\rm ex}^{PP}$, $\boldsymbol{\Pi}^{PQ}$, $\boldsymbol{V}_{\rm ex}^{PQ}$, $\boldsymbol{\Pi}^{QP}$, $\boldsymbol{V}_{\rm ex}^{QP}$, $\mathbf{S}^{QQ}$, $\mathbf{S}^{PP}$, $\boldsymbol{V}_{\rm d}^{QQ}$, and $\boldsymbol{V}_{\rm ex}^{QQ}$ are all $N\times N$ matrices. These matrix elements are given as follows:

$$V_{ij}^{PP}=V_{ij}^{QQ}=\int B_{i,k}(r)V(r)B_{j,k}(r)\,{\rm d}r, \tag{10}$$

$$S_{ij}^{PP}=S_{ij}^{QQ}=\int B_{i,k}(r)B_{j,k}(r)\,{\rm d}r, \tag{11}$$

$$\Pi_{ij}^{PQ}=c\int B_{i,k}(r)\left(\frac{\kappa}{r}-\frac{\rm d}{{\rm d}r}\right)B_{j,k}(r)\,{\rm d}r, \tag{12}$$

$$\Pi_{ij}^{QP}=c\int B_{i,k}(r)\left(\frac{\kappa}{r}+\frac{\rm d}{{\rm d}r}\right)B_{j,k}(r)\,{\rm d}r, \tag{13}$$

$$V_{{\rm d}ij}^{PP}=V_{dij}^{QQ}=\sum_b(2j_b+1)\delta(k,0)\times\sum_k\int B_{i,k}(r_1)B_{j,k}(r_1)\,{\rm d}r_1\times\int\frac{r_<^k}{r_>^{k+1}}\left(P_b^2(r_2)+Q_b^2(r_2)\right){\rm d}r_2, \tag{14}$$

$$V_{{\rm ex}ij}^{PP}=\sum_b(2j_b+1)\sum_k\begin{pmatrix}j_\kappa & k & j_b\\ -1/2 & 0 & 1/2\end{pmatrix}^2\times\int B_{i,k}(r_1)P_b(r_1)\,{\rm d}r_1\times\int\frac{r_<^k}{r_>^{k+1}}P_b(r_2)B_{j,k}(r_2)\,{\rm d}r_2, \tag{15}$$

$$V_{{\rm ex}ij}^{PQ}=V_{{\rm ex}ij}^{QP}=\sum_b(2j_b+1)\sum_k\begin{pmatrix}j_\kappa & k & j_b\\ -1/2 & 0 & 1/2\end{pmatrix}^2\times\int B_{i,k}(r_1)P_b(r_1)\,{\rm d}r_1\times\int\frac{r_<^k}{r_>^{k+1}}Q_b(r_2)B_{j,k}(r_2)\,{\rm d}r_2, \tag{16}$$

$$V_{\mathrm{ex}ij}^{QQ} = \sum_b (2j_b+1)\sum_k \begin{pmatrix} j_\kappa & k & j_b \\ -1/2 & 0 & 1/2 \end{pmatrix}^2 \times \int B_{i,k}(r_1)Q_b(r_1)\,\mathrm{d}r_1 \times \int \frac{r_<^k}{r_>^{k+1}} Q_b(r_2)B_{j,k}(r_2)\,\mathrm{d}r_2, \quad (17)$$

where b represents the atomic core orbital, V is the Coulomb potential between electrons and nucleus, and V_{d} and V_{ex} are the direct and exchange interactions among atomic core electrons, respectively. A' are the boundary conditions, and the explicit expression can be found in Ref. [33]. In our calculations, matrix elements are evaluated by using Gaussian–Legendre quadratures. In the present work, we solve DF equation using a completely self-consistent iteration method based on B-spline basis set. While, in Ref. [33], DF equation was solved firstly by using a point-by-point numerical integration scheme, matrix A was then constructed by combining the obtained core DF orbitals with a B-spline basis set.

Here, an Rb atom is set as a representative of alkali metal atoms. In Table 1, the single particle orbital energies and the total energy of the close shell Rb^+ are presented and compared with the numerical results obtained using General Relativistic Atomic Structure Program (GRASP).[34] Our results have the agreement of at least six significant digits with GRASP results. In the present calculations, 50 B-splines of $k = 7$ order are used. $R_{\max}$ is set as 80 a.u. A Fermi nuclear model is adopted.

Table 1. The single particle orbital energies and the total energies of the close shell Rb^+.

Orbital	B-spline	GRASP
$1s_{1/2}$	−562.3368228	−562.3368234
$2s_{1/2}$	−77.7052730	−77.7052739
$3s_{1/2}$	−12.7632419	−12.7632427
$4s_{1/2}$	−1.7671144	−1.7671149
$2p_{1/2}$	−70.2205919	−70.2205935
$3p_{1/2}$	−10.0221392	−10.0221405
$4p_{1/2}$	−1.0337650	−1.0337651
$2p_{3/2}$	−67.9683284	−67.9683279
$3p_{3/2}$	−9.6687416	−9.6687411
$4p_{3/2}$	−0.9976364	−0.9976363
$3d_{3/2}$	−4.8796796	−4.8796798
$3d_{5/2}$	−4.8196506	−4.8196508
Total	−2979.6652150	−2979.6652173

2.2. Polarization potential

The second step of the present method is that a semi-empirical core polarization potential is introduced to approximate the correlation interaction between the core electrons and the valence electron. The effective potential of the valence electron with the core is then written as

$$V_{\mathrm{core}}(\boldsymbol{r}) = V_{\mathrm{dir}}(\boldsymbol{r}) + V_{\mathrm{exc}}(\boldsymbol{r}) + V_{\mathrm{pol}}(\boldsymbol{r}). \quad (18)$$

Where $V_{\mathrm{dir}}(\boldsymbol{r})$ and $V_{\mathrm{exc}}(\boldsymbol{r})$ are the direct and exchange interactions of the valence electron with the DF core, respectively. The ℓ-dependent polarization potential,[24] V_{pol}, is semi-empirical with the functional form:

$$V_{\mathrm{pol}}(r) = -\sum_{\ell j} \frac{\alpha_{\mathrm{core}}^{(\ell)} g_{\ell j}^2(r)}{2r^4} |\ell j\rangle\langle \ell j|. \quad (19)$$

The coefficient, α_{core} is the static dipole polarizability of the core and $g_{\ell j}^2(r) = 1 - \exp\left(-r^6/\rho_{\ell,j}^6\right)$ is a cutoff function designed to make the polarization potential finite at the origin. The cutoff parameters, $\rho_{\ell,j}$ are tuned to reproduce the binding energies of the ns, np_J, and $nd_{J'}$ states, and ensure that the calculated energies have at least four significant digits, which is the same as the NIST database.[35] This kind of calculation with the core-polarization potential is called a Dirac–Fock plus core polarization (DFCP) model.

3. Numerical results and discussion

3.1. Polarizability

The static 2^ℓ-pole ($\ell = 1,2,3$) polarizability for an atomic state ψ_0 comes from three parts

$$\alpha^{(\ell)} = \alpha_c^{(\ell)} + \alpha_{cv}^{(\ell)} + \alpha_v^{(\ell)}. \quad (20)$$

$\alpha_v^{(\ell)}$ represents the valence contribution, which can be obtained by a sum over all intermediate states

$$\alpha_v^{(\ell)} = \frac{2}{(2\ell+1)(2j_0+1)} \sum_{n\neq 0} \frac{|\langle \psi_n \| Q_0^{(\ell)} \| \psi_0 \rangle|^2}{\varepsilon_{n0}}. \quad (21)$$

Here, $\varepsilon_{n0} = \varepsilon_n - \varepsilon_0$, and the experimental energies[35] are used in our calculations. $Q_0^{(\ell)}$ is electron multipole transition operator. The contributions of core excited states $\alpha_c^{(\ell)}$ can be written as

$$\alpha_{\mathrm{c}}^{(\ell)} = \sum_i \frac{\ell N_i \langle r_i^{2\ell-2}\rangle}{(\varepsilon_i + \Delta^{(\ell)})^2}, \quad (22)$$

where ε_i, N_i, and $\langle r_i^{2\ell-2}\rangle$ are single particle orbital energy, the number of electrons, and the mean values of $r^{2\ell-2}$ of the i-th closed subshell, respectively. The energy parameters $\Delta^{(\ell)}$ are tuned to reproduce the experimentally known core polarizability. These energy parameters are required in the calculations of dynamic polarizabilities and dispersion coefficients. In Table 2, the energies parameters $\Delta^{(\ell=1,2)}$, cutoff parameters ρ, and core polarizabilities $\alpha_{\mathrm{core}}^{(\ell=1,2)}$ are given. It should be mentioned that, $\alpha_{\mathrm{core}}^{(2)}$ of Fr is not available in the literature. $\alpha_{\mathrm{core}}^{(2)} = 100$ is used in the present work. The contribution of $\alpha_{\mathrm{core}}^{(2)}$ to $\alpha^{(2)}$ of the atomic Fr is less than 1.5%. The contribution of $\alpha_{cv}^{(\ell)}$ is neglected because it is too small.[22,23]

Table 2. The core polarizabilities, energy parameters, and cut-off parameters for alkali metal atoms.

Parameters	Li	Na	K	Rb	Cs	Fr
$\alpha^{(1)}_{\rm core}$	0.1925[37]	0.99[28]	5.47[38]	9.1[36]	15.8[39]	20.4[40]
$\alpha^{(2)}_{\rm core}$	0.114[37]	1.52[36]	16.27[36]	35.4[36]	86[22]	100
$\Delta^{(1)}$	0.4300	0.8395	0.0600	0.1335	0.1915	0.2000
$\Delta^{(2)}$	−1.1430	−0.9044	−0.2325	−0.1164	−2.0970	−3.2835
$\rho_{s_{1/2}}$	1.3915	1.4312	2.1128	2.4243	2.7720	3.1398
$\rho_{p_{1/2}}$	1.2625	1.5925	2.0152	2.3425	2.6500	2.9821
$\rho_{p_{3/2}}$	1.2625	1.5455	2.0106	2.2965	2.6680	2.9700
$\rho_{d_{3/2}}$	1.2625	1.6501	2.3446	2.8043	3.1930	3.3600
$\rho_{d_{5/2}}$	1.2625	1.6501	2.3479	2.8224	3.2370	3.5033

The dipole polarizability has a tensor component for states with $J > 1/2$,

$$\alpha_t^{(1)} = 4\left[\frac{5J(2J-1)}{6(J+1)(2J+1)(2J+3)}\right]^{1/2} \times \sum_n (-1)^{J+J_n} \begin{Bmatrix} J & 1 & J_n \\ 1 & J & 2 \end{Bmatrix} \frac{|\langle\psi_n\|Q_0^{(1)}\|\psi_0\rangle|^2}{\varepsilon_{n0}}. \quad (23)$$

In the calculations, the electron multipole transition operator should include a polarization correction. The modified transition operator is

$$Q_0^{(\ell)} = r^{(\ell)}C^{(\ell)}\left(1 - \frac{\alpha^{(\ell)}_{\rm core}}{r^{(2\ell+1)}}\left(1-\exp(-r^6/\rho^6)\right)^{1/2}\right). \quad (24)$$

The cutoff parameter ρ used in Eq. (24) is set to $\rho = (\rho_{\ell_a,j_a} + \rho_{\ell_b,j_b})/2$ where a,b refer to the initial and final states of the transition.

In Table 3, the static multipolar polarizabilities of the ground states for alkali metal atoms are presented and compared with those obtained from other methods and the available experimental measurements. For an Li atom, the biggest difference between our results and the high-precision nonrelativistic Hylleraas results by Tang *et al.*[41] are less than 0.1%. Three many-body methods, DFCP, RMBPT, and CICP, give almost the same precision results. For the dipole polarizabilities of Li, Na, K, and Rb, our results are in agreement with experiments considering their uncertainties.[14,16,17] For the dipole polarizability of a Cs atom, our results are smaller than the experimental result by about 1%.[18] Our result of the dipole polarizability for Fr is smaller than RMBPT result by about 2%. At the same time, it can be noted that the dipole polarizability of Fr is smaller than Cs, which does not consist with the trend from Na to Cs. For the quadrupole and octupole polarizabilities, one can find that our DFCP method gives almost the same results as *ab initio* RMBPT method.[22,23]

In Table 4, the static scalar polarizabilities of the first seven excited states for alkali metal atoms are presented and compared with experimental values and other theoretical results. It can be noted that our results of the excited states for Li, Na, K, and Rb are consistent with all-order method,[42,50,53] RCCSD(T),[43] RMBPT[47] results, and the available experimental values considering their uncertainties.[13,16,45,46,48,49,51,52] For Cs atoms, our results are in agreement with all-order results[54] and the experimental values[55–59] in their uncertainties. The polarizabilities of the excited states for Fr atom, to our knowledge, are the first reported results.

Table 3. The static dipolar, quadrupole, and octupole polatizabilities of the ground states for alkali metal atoms. The experimental energies[35] were adopted in our calculations.

		$\alpha^{(1)}$	$\alpha^{(2)}\times10^{-3}$	$\alpha^{(3)}\times10^{-4}$
Li	Present	164.19	1.4241	3.9677
	RMBPT	164.0[23]	1.424[22]	3.957[22]
	CICP[24]	164.21	1.4243	3.968
	Hylleraas[41]	164.112(1)	1.423263(3)	3.964929(2)
	Expt.[13]	164.0(3.4)		
	Expt.[14]	164.2(1.1)		
Na	Present	162.71	1.8782	5.5487
	RMBPT	162.6[23]	1.885[22]	5.54[22]
	CICP[24]	162.8	1.879	5.552
	Expt.[16]	162.7(8)		
K	Present	289.76	5.0011	17.746
	RMBPT	290.2[23]	5.000[22]	17.7[22]
	CICP[24]	290.0	5.005	17.77
	Expt.[17]	290.8(1.4)		
Rb	Present	317.62	6.4810	23.783
	RMBPT	318.6[23]	6.520[22]	23.7[22]
	CICP[24]	315.7	6.480	23.78
	Expt.[17]	318.8(1.4)		
Cs	Presemt	396.32	10.395	39.622
	RMBPT	399.8[23]	10.47[22]	39.5[22]
	Expt.[18]	401.0(6)		
Fr	Present	312.94	8.6535	32.327
	RMBPT[23]	317.8/313		

Table 4. The static scalar dipolar polarizability of the first seven excited states for alkali metal atoms.

Atoms	Levels						
Li	$2p_{1/2}$	$2p_{3/2}$	$3s_{1/2}$	$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
Present	126.97	126.99	4132.7	28240	28268	−14914	−14933
All-order[42]	126.97	126.98	4130	28255	28261	−14925	−14928
RCCSD(T)[43]	127.15	127.09	4116	28170	28170	−14820	−14930
Hylleraas	126.9458(3)[41]		4131.32(1)[44]			−14928.230(5)[41]	
Expt.		126.87(36)[45]					−15130(40)[46]
Na	$3p_{1/2}$	$3p_{3/2}$	$4s_{1/2}$	$4p_{1/2}$	$4p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
Present	360.05	361.67	3102.6	−4488.5	−4420.3	6419.5	6395.7
RMBPT[47]	359.6	361.4					
Expt.	359.6(7)[48]	360.7(8)[49]					
K	$4p_{1/2}$	$4p_{3/2}$	$5s_{1/2}$	$5p_{1/2}$	$5p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
Present	608.90	619.43	4968.7	7052.1	7219.8	1426.2	1417.0
All-order[50]	611(6)	620(5)	4961(22)	7053(70)	7230(61)	1420(30)	1412(31)
RMBPT[47]	605	616					
Expt.	610(6)[51]	615(7)[52]					
Rb	$5p_{1/2}$	$5p_{3/2}$	$6s_{1/2}$	$6p_{1/2}$	$6p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$
Present	811.64	874.05	5174.6	12406	13431	582.55	548.90
All-order[53]	814(8)	875(7)	5169(21)	12420(120)	13440(70)	574(25)	541(26)
RMBPT[47]	807	870					
Expt.	811(6)[51]	857(7)[52]					
Cs	$6p_{1/2}$	$6p_{3/2}$	$7s_{1/2}$	$7p_{1/2}$	$7p_{3/2}$	$5d_{3/2}$	$5d_{5/2}$
Present	1332.2	1644.7	6242.5	30138	37867	−346.30	−450.30
All-order[54]	1338(54)	1648(58)	6238(41)	29900	37500	−352(69)	−453(70)
Expt.	1328.4(6)[55]	1641(2)[56]	6238(6)[57]	29600(600)[58]	37900(800)[59]		
Fr	$7p_{1/2}$	$7p_{3/2}$	$8s_{1/2}$	$8p_{1/2}$	$8p_{3/2}$	$6d_{3/2}$	$6d_{5/2}$
Present	1171.8	2207.4	4789.1	22782	43617	−254.71	−610.31

Table 5. The static tensor dipolar polarizability of $p_{3/2}$, $d_{3/2}$, $d_{5/2}$ excited states for alkali metal atoms.

Systems	Levels			
Li	$2p_{3/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
Present	1.6333	−2172.8	11399	16303
All-order[42]	1.610	−2170	11405	16297
RCCSD(T)[43]	1.597	−2160	11460	16290
Hylleraas[41]	1.6214(3)			16297.675(5)
Expt.	1.64(4)[45]			16430(60)[46]
Na	$3p_{3/2}$	$4p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
Present	−88.364	−168.43	−3566.5	−5063.7
RMBPT[47]	−88.0			
Expt.[49]	−88.4			
K	$4p_{3/2}$	$5p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$
Present	−109.87	−1058.4	−483.98	−676.55
All-order[50]	−109.4(1.1)	−1065(18)	−482(19)	−673(23)
RMBPT[47]	−111			
Expt.[51]	−107(2)			
Rb	$5p_{3/2}$	$6p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$
Present	−168.40	−2067.4	−55.292	−30.071
All-order[53]	−167(2)	−2075(21)	−51(6)	−24(9)
RMBPT[47]	−171			
Expt.[51]	−163(3)			
Cs	$6p_{3/2}$	$7p_{3/2}$	$5d_{3/2}$	$5d_{5/2}$
Present	−262.95	−4431.9	359.26	680.47
All-order[54]	−261(13)	−4410(170)	370(28)	691(40)
Expt.	−262.4(1.5)[56]	−4000(80)[58]		
		−4330(170)[59]		
		−4430(120)[60]		
Fr	$7p_{3/2}$	$8p_{3/2}$	$6d_{3/2}$	$6d_{5/2}$
Present	−452.28	−6585.9	230.85	889.45

In Table 5, the corresponding tensor polarizablities of the excited states with $j > 1/2$ are presented and compared with all-order,[42,50,53,54] RCCSD(T),[43] RMBPT methods,[47] and available experimental results.[45,46,49,51,56,58–60] It can be noted that the biggest difference among the other theoretical results considering their uncertainties and ours is less than 1%. While, for the $3d_{5/2}$ state of Li, the experimental value is bigger than all the theoretical results by about 100 a.u.[41–43] A more precise experiment is needed to clarify this difference.

3.2. Dispersion coefficient

The long range van der Waals interaction between two spherically symmetric atoms (a, b) in the ground state can be represented as[61]

$$V^{ab}(R) = -\sum_{n=3} \frac{C_{2n}^{ab}}{R^{2n}}, \tag{25}$$

where R is internuclear distance and C_{2n}^{ab} are the two-body dispersion coefficients. The two body dispersion coefficients can be given by an integral over imaginary photon frequencies of the produce of the multipole dynamic polarizabilities for interaction atoms[62]

$$C_{2n}^{ab} = \frac{(2n-2)!}{2\pi} \sum_{\ell_a=1}^{n-2} \frac{1}{(2\ell_a)!(2\ell_b)!} \times \int_0^\infty \alpha_a^{(\ell_a)}(\mathrm{i}\omega)\alpha_b^{(\ell_b)}(\mathrm{i}\omega)\mathrm{d}\omega, \quad \ell_a + \ell_b = n-1. \tag{26}$$

Here $\alpha_a^{(\ell_a)}(\mathrm{i}\omega)$ represents the 2^{ℓ_a}-pole dynamic polarizabilities at imaginary frequency $\mathrm{i}\omega$ of the ground states for atom a. It is defined as

$$\alpha^{(\ell)}(\mathrm{i}\omega) = 2\mathrm{Re}\left(\sum_n \frac{|\langle\psi_n|Q_0^{(\ell)}|\psi_0\rangle|^2}{\varepsilon_{k0}+\mathrm{i}\omega}\right) = \frac{2}{(2\ell+1)(2j_0+1)}\sum_n \frac{|\langle\psi_n\|Q_0^{(\ell)}\|\psi_0\rangle|^2\varepsilon_{k0}}{\varepsilon_{k0}^2+\omega^2}. \quad (27)$$

In this work, the integral of Eq. (26) is evaluated by the Gaussian quadratures method. We used the same Gauss points and weights as Ref. [23]. The dynamic polarizabilities were evaluated with the same sets of matrix elements and energies as the static polarizabilities.

In Table 6, the two-body dispersion coefficients of the ground states for alkali metal atoms are presented and compared with other theoretical methods. For the lighter atoms Li, Na, and K, the differences among DFCP, CICP,[24] and RMBPT[22,23] are less than 1%. For Rb and Cs atoms, the largest difference between DFCP and RMBPT methods is no more than 3%. For the heavier Fr atom, our results of C_6 for the interactions between Fr and other atoms are smaller than the RMBPT[22,23] results by about 2%. This difference stems from our results of dipole polarizbilities for Fr, which are 2% smaller than the RMBPT method. To the best of our knowledge, the C_8 and C_{10} results of Fr are the first results to be reported. From Table 3, 4, 5, 6, one can easily note that DFCP method can work in heavier atom systems than the CICP method.

Table 6. Two-body dispersion coefficients C_6, C_8, and C_{10} for homo-nuclear and hetero-nuclear alkali-metal interactions.

	$C_6\times10^{-3}$			$C_8\times10^{-4}$			$C_{10}\times10^{-6}$		
	DFCP	RMBPT[23]	CICP[24]	DFCP	RMBPT[22]	CICP[24]	DFCP	RMBPT[22]	CICP[24]
Li–Li	1.394	1.389(2)	1.3946	8.351	8.34	8.351	7.38	7.35	7.381
Li–Na	1.471	1.467(2)	1.472	9.881	9.88	9.888	9.18	9.16	9.187
Li–K	2.325	2.322(5	2.328	19.53	19.5	19.5	21.0	21.0	21.01
Li–Rb	2.535	2.545(7)	2.533	23.29	23.4	23.29	26.0	26.1	26.08
Li–Cs	3.046	3.065(17)		32.01	32.1		38.3	38.4	
Li–Fr	2.645	2.682(23)		28.05			32.9		
Na–Na	1.560	1.556(4)	1.561	11.57	11.60	11.59	11.3	11.3	11.34
Na–K	2.449	2.447(6)	2.454	22.36	22.4	22.40	25.2	25.3	25.32
Na–Rb	2.673	2.683(7)	2.672	26.47	26.6	26.49	31.1	31.3	31.22
Na–Cs	3.208	3.227(18)		35.95	36.2		45.3	45.5	
Na–Fr	2.803	2.842(24)		31.56			39.1		
K–K	3.895	3.897(15)	3.905	41.88	42.0	41.97	53.6	53.7	53.74
K–Rb	4.252	4.274(13)	4.253	49.01	49.3	49.04	65.2	66	65.34
K–Cs	5.120	5.159(30)		65.69	66.2		93.0	94	
K–Fr	4.434	4.500(39)		57.34			80.5		
Rb–Rb	4.644	4.690(23)	4.635	57.07	57.7	57.01	79.0	79.6	79.16
Rb–Cs	5.594	5.663(34)		75.99	76.9		112	113	
Rb–Fr	4.851	4.946(44)		66.28			97.1		
Cs–Cs	6.746	6.846(74)		100.4	102		158	159	
Cs–Fr	5.838	5.968(60)		872.3			137		
Fr–Fr	5.104	5.256(89)		760.7			119		

4. Summary

A relativistic atomic structure model, DFCP method, has been developed and applied to the calculations on the static polarizabilties and two-body dispersion coefficients of alkali metal atoms. This method starts from the solution of Dirac–Fock equation for close shell atomic system. A semi-empirical core polarization potential is then introduced to approximate the core–valence electron correction. A comparison of our results with those obtained from *ab initio* all-order, RCCSD, and RMBPT methods reveal a good level of agreement. Compared with non-relativistic CICP method, the DFCP method can be applied to heavier atomic systems and they predict the properties of spin-orbital doublet in a natural way. Although at the present stage the DFCP method for monovalent system has been developed, it can easily be expanded and applied to diva-

lent and even multivalent systems if the configuration interaction method is combined.

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References

[1] Madej A A, Dube P, Zhou Z, Bernard J E and Gertsvolf M 2012 *Phys. Rev. Lett.* **109** 203002
[2] Chou C W, Hume D B, Koelemeij J C J, Wineland D J and Rosenband T 2010 *Phys. Rev. Lett.* **104** 070802
[3] Derevianko A and Katori H 2011 *Rev. Mod. Phys.* **83** 331
[4] Hinkley N, Sherman J A, Phillips N B, Schioppo M, Lemke N D, Beloy K, Pizzocaro M, Oates C W and Ludlow A D 2013 *Science* **341** 1215
[5] Zhou M, Chen N, Zhang X H, Huang L Y, Yao M F, Tian J, Gao Q, Jiang H L, Tang H Y and Xu X Y 2013 *Chin. Phys. B* **22** 103701
[6] Holmgren W F, Trubko R, Hromada I and Cronin A D 2012 *Phys. Rev. Lett.* **109** 243004
[7] Tang Y B, Qiao H X, Shi T Y and Mitroy J 2013 *Phys. Rev. A* **87** 042517
[8] Weiner J, Bagnato V S, Zilio S and Julienne P S 1999 *Rev. Mod. Phys.* **71** 1
[9] Leggett A J 2001 *Rev. Mod. Phys.* **73** 307
[10] Jones K M, Tiesinga E, Lett P D and Julienne P S 2006 *Rev. Mod. Phys.* **78** 483
[11] Arora B, Safronova M S and Clark C W 2011 *Phys. Rev. A* **84** 043401
[12] LeBlanc L J and Thywissen J H 2007 *Phys. Rev. A* **75** 053612
[13] Molof R W, Schwartz H L, Miller T M and Bederson B 1974 *Phys. Rev. A* **10** 1131
[14] Hall W D and Zorn J C 1974 *Phys. Rev. A* **10** 1141
[15] Miffre A, Jacquey M, Büchner M, Trénec G and Vigué J 2006 *Phys. Rev. A* **73** 011603
[16] Ekstrom C R, Schmiedmayer J, Chapman M S, Hammond T D and Pritchard D E 1995 *Phys. Rev. A* **51** 3883
[17] Holmgren W F, Revelle M C, Lonij V P A and Cronin A D 2010 *Phys. Rev. A* **81** 053607
[18] Amini J M and Gould H 2003 *Phys. Rev. Lett.* **91** 153001
[19] Mitroy J, Safronova M S and Clark C W 2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 202001
[20] Safronova U I 2010 *Phys. Rev. A* **82** 022504
[21] Sahoo B K and Das B P 2008 *Phys. Rev. A* **77** 062516
[22] Porsev S G and Derevianko A 2003 *J. Chem. Phys.* **119** 844
[23] Derevianko A, Porsev S G and Babb J F 2010 *At. Data Nucl. Data Tables* **96** 323
[24] Mitroy J and Bromley M W J 2003 *Phys. Rev. A* **68** 052714
[25] Huang S Z and Sun Q F 2011 *J. Chem. Phys.* **134** 144110
[26] Ye A and Wang G 2008 *Phys. Rev. A* **78** 014502
[27] Guo K, Wang G and Ye A 2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 135004
[28] Müller W, Flesch J and Meyer W 1984 *J. Chem. Phys.* **80** 3297
[29] Tang Y B, Zhong Z X, Li C B, Qiao H X and Shi T Y 2013 *Phys. Rev. A* **87** 022510
[30] Zhang Y H, Tang L Y, Zhang X Z, Shi T Y and Mitroy J 2012 *Chin. Phys. Lett.* **29** 063101
[31] Tang L Y, Tang Y B, Shi T Y and Mitroy J 2013 *J. Chem. Phys.* **139** 134112
[32] Bachau H, Cormier E, Decleva P, Hansen J E and Martin F 2001 *Rep. Prog. Phys.* **64** 1815
[33] Johnson W R, Blundell S A and Sapirstein J 1988 *Phys. Rev. A* **37** 307
[34] Parpia F A, Fischer F C and Grant I P 1996 *Comput. Phys. Commun.* **94** 249
[35] Kramida A, Ralchenko Y, Reader J and NIST ASD Team 2012 *NIST Atomic Spectra Database* (version 5.0.0)
[36] Johnson W R, Kolb D and Huang K 1983 *At. Data Nucl. Data Tables* **28** 333
[37] Tang L Y, Zhang J Y, Yan Z C, Shi T Y and Mitroy J 2010 *J. Chem. Phys.* **133** 104306
[38] Opik U 1967 *Proc. Phys. Soc. London* **92** 566
[39] Derevianko A and Porsev S G 2002 *Phys. Rev. A* **65** 053403
[40] Safronova U I, Johnson W R and Safronova M S 2007 *Phys. Rev. A* **76** 042504
[41] Tang L Y, Yan Z C, Shi T Y and Babb J F 2009 *Phys. Rev. A* **79** 062712
[42] Safronova M S, Safronova U I and Clark C W 2012 *Phys. Rev. A* **86** 042505
[43] Wansbeek L W, Sahoo B K, Timmermans R G E, Das B P and Mukherjee D 2010 *Phys. Rev. A* **82** 029901
[44] Tang L Y, Bromley M W J, Yan Z C and Mitroy J 2013 *Phys. Rev. A* **87** 032507
[45] Windholz L, Musso M, Zerza G and Jäger H 1992 *Phys. Rev. A* **46** 5812
[46] Ashby R, Clarke J J and van Wijingaarden W A 2003 *Eur. Phys. J. D* **23** 327
[47] Zhu C, Dalgarno A, Porsev S G and Derevianko A 2004 *Phys. Rev. A* **70** 032722
[48] Windholz L and Neureiter C 1985 *Phys. Lett. A* **109** 155
[49] Windholz L and Musso M 1989 *Phys. Rev. A* **39** 2472
[50] Safronova M S, Safronova U I and Clark C W 2013 *Phys. Rev. A* **87** 052504
[51] Krenn C, Scherf W, Khait O, Musso M and Windholz L 1997 *Z. Phys. D: At. Mol. Clusters* **41** 229
[52] Miller K E, Krause D and Hunter L R 1994 *Phys. Rev. A* **49** 5128
[53] Safronova M S and Safronova U I 2011 *Phys. Rev. A* **83** 052508
[54] Iskrenova-Tchoukova E, Safronova M S and Safronova U I 2007 *J. Comput. Methods Sci. Eng.* **7** 521
[55] Hunter L R, Krause D, Miller K E, Berkeland D J and Boshier M G 1992 *Optica Spektrosk* **94** 210
[56] Tanner C and Wieman C 1988 *Phys. Rev. A* **38** 162
[57] Bennett S C, Roberts J L and Wieman C E 1999 *Phys. Rev. A* **59** R16
[58] Domelunksen V 1983 *Optica Spektrosk* **54** 950
[59] Khadjavi A, Lurio A and Happer W 1968 *Phys. Rev. A* **167** 128
[60] Khvoshtenko G and Chaika M 1968 *Optica Spektrosk* **25** 246
[61] Dalgarno A and Davison W D 1966 *Advances in Atomic and Molecular Physics*, ed. Bates R D and Estermann I (New York/London: Academic Press)
[62] Patil S H and Tang K T 1997 *J. Chem. Phys.* **106** 2298