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A simple model potential description of the alkaline earth isoelectronic sequences

S.H. Patil[a]

Department of Physics, Indian Institute of Technology, Bombay 400 076, India
and
Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, 37073 Göttingen, Germany

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Abstract. We have developed a simple model potential with a hard core and the correct large-r Coulombic behaviour, to describe the interaction of an electron with a closed shell. One has an exact, analytic ground state wave function for this potential. This potential is used to develop two-electron perturbed and unperturbed wave functions, with the correct asymptotic behaviour and cusp conditions. These wave functions allow us to obtain accurate values for the two-electron energies, polarisabilities, hyperpolarisabilities, and dispersion coefficients of alkaline earth sequences. Many of these results are the only ones available in the literature.

PACS. 31.15.-p Calculations and mathematical techniques in atomic and molecular physics (excluding electron correlation calculations)

1 Introduction

The analysis of the properties of He and its isoelectronic ions provides a simple but important and interesting example of the many body problems. On the one hand it illustrates the serious complications introduced by the many-variable, non-separable Schroedinger equation. On the other hand, it motivates us to consider some specific properties of the differential equation and its solution, which provide useful insight into its structure. As such the helium atom and its isoelectronic ions have been analysed from different perspectives, apart from the very elaborate variational approach [1–5]. For example, the usual one parameter variational solution suggests an idea of the screening of the nuclear charges. More recently, it has been emphasised [6–11] that wave functions which incorporate some specific properties of the exact wave functions, provide accurate and useful representations of the energy eigenstates of two-electron atoms and ions. In particular, the behaviour of the wave function when two particles are close to each other, or when one of the particles is far away, has been found to be an important component of the wave function. These considerations need to be extended to other systems.

The alkaline earth sequences are in some ways similar to the two-electron atoms and ions. They have two electrons outside the closed shells. However, the interaction of these two electrons with the closed-shell core is more complicated than a simple Coulombic term. One may attempt to simulate this interaction by a model potential and then deduce the properties of the system by analysing the wave function of the two electrons in this model potential. Effectively, the problem is then reduced to that of a helium atom except that the Coulombic interaction of the two electrons with the nucleus is replaced by a model potential. Such an approach has been considered but with limited success. An ℓ-dependent, model potential with several parameters was used [12] to obtain the polarisabilities and dispersion coefficients of Be, Mg, and Ca. Though the analysis demonstrated the importance of the correlation between the two outer electrons, it was confined only to these three alkaline earth atoms, and the complicated model potential and the numerical solutions do not provide any insight into the structure of the perturbed or unperturbed wave functions.

Here, we propose a simple model potential for the interaction of an electron with a closed-shell core. It has the nice property that in addition to giving the correct 1-electron ground-state energy, it has a simple, two-term ground-state wave function. We then develop two-electron wave functions based on the correct asymptotic behaviour and the correct cusp condition. Incorporation of these properties allows us to obtain simple, but very accurate wave functions for the two-electron ground states with only one variational parameter. The energies obtained from these wave functions are in agreement with the experimental values to within 1% for all the alkaline earth sequence members with charges $-1, 0, 1, 2$. These wave functions are then used to obtain simple, analytic expressions for perturbations in the wave functions and energies

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[a] e-mail: `sharad@phy.iitb.ernet.in`

in the presence of multipolar potentials. These expressions for the perturbed wave functions allow us to deduce multipolar polarisabilities, hyperpolarisabilities for all the sequences, and the dispersion coefficients for the neutral atoms. Some of these quantities are new, and should be of considerable importance in the analysis of the interactions of alkaline-earth sequences with each other and with other systems. Unless stated otherwise, we will use atomic units in our description.

2 A model one-electron potential

We first develop a simple, model potential which is intuitively appealing, has the correct Coulombic behaviour at large distances, and which incorporates a ground state with the appropriate energy.

Consider a potential of the form

$$V_0 = -\frac{Z}{r} + \frac{\ell_2(\ell_2+1)}{2r^2}\cdot \tag{2.1}$$

It may be noted that the $1/r^2$ term here is a part of the potential, and is not the angular momentum barrier term. Its coefficient is written as $l_2(l_2+1)/2$ so that one can write the s-wave energy eigenvalues and eigenfunctions in a simple, closed form in terms of l_2 which in general is not an integer. In particular one has the s-wave energies

$$E = -\frac{Z^2}{2(\ell_2+n)^2}, \quad n = 1, 2, ... \tag{2.2}$$

and the corresponding wave functions are

$$\psi(r) = N r^{\ell_2}\, {}_1F_1(\ell_2+1-\frac{Z}{a_2}, 2\ell_2+2, 2a_2 r)\mathrm{e}^{-a_2 r} \tag{2.3}$$

$$a_2 = (-2E_2)^{1/2}$$

with N being the normalization constant, where ${}_1F_1(a,b,z)$ is the confluent hypergeometric function. The first excited state of this set has an energy

$$E_2 = -\frac{Z^2}{2(\ell_2+2)^2} \tag{2.4}$$

and the corresponding eigenfunction has a node or zero at

$$R = \frac{\ell_2+1}{a_2}\cdot \tag{2.5}$$

This energy and the eigenfunction will therefore, also correspond to the ground state of the potential in equation (2.1) but with an additional, infinite potential barrier for $r < R$. Now for an electron outside a closed shell core, because of the exclusion principle, there is very little penetration into the core. Therefore, a potential with a Coulombic behaviour at large r, and an infinite potential barrier for $r < R$, would be quite appropriate for the description of the properties of an electron outside a closed shell.

For the description of the properties of the alkaline earth sequences, we propose a model potential to describe the electron-core interaction

$$\begin{aligned} V_2(r) &= -\frac{Q}{r} + \frac{\ell_2(\ell_2+1)}{2r^2} && \text{for} \quad r > R \\ &= \infty && \text{for} \quad r \le R \end{aligned} \tag{2.6}$$

where Q is the core charge and ℓ_2 and R are determined in terms of the second ionisation energy $-E_2$ of the sequence,

$$\begin{aligned} \ell_2 &= \frac{Q}{a_2} - 2, \quad a_2 = (-2E_2)^{1/2} \\ R &= \frac{\ell_2+1}{a_2}\cdot \end{aligned} \tag{2.7}$$

For example, for the description of the properties of Be, we have $Q = 2$ and $E_2 = -18.2112/27.2114$, where 18.2112 eV is the second ionisation energy of Be. The ground state of this potential is described by the wave function

$$\begin{aligned} \phi_2(r) &= N_2(r-R)r^{\ell_2}\mathrm{e}^{-a_2 r} && \text{for} \quad r > R \\ &= 0 && \text{for} \quad r \le R \end{aligned} \tag{2.8}$$

where N_2 is the normalization constant.

The 1-electron, s-wave spectra of our model potential with the ionisation energy as the only input are in close agreement with the experimental s-wave spectra of alkali sequences. For example, the energies of the excited s-wave states of Na and Ba$^+$ predicted are -1.950,-1.024 eV and -4.77, -2.80 eV, whereas the corresponding experimental energies are -1.948,-1.023 eV and -4.751,-2.809 eV respectively. Even the predicted energies of the $\ell = 1$ states are generally within about 10% of the experimental values of the energies. This is adequate for our purpose of using this potential for the description of two-electron states. The reason for this is that when one of the electrons, say electron 1, is in $\ell = 1$ state, it is farther away and its main interaction is with the inner electron and the Coulombic part of the interaction with the core.

3 Ground-state properties of alkaline earth sequences

We propose that the ground-state properties of the two outer electrons in the alkaline earth sequence are described by the Hamiltonian

$$H = \frac{1}{2}p_1^2 + \frac{1}{2}p_2^2 + V_2(r_1) + V_2(r_2) + \frac{1}{r_{12}} \tag{3.1}$$

$$\begin{aligned} V_2(r_i) &= -\frac{Q}{r_i} + \frac{\ell_2(\ell_2+1)}{2r_i^2} && \text{for} \quad r_i > R \\ &= \infty && \text{for} \quad r_i \le R \end{aligned}$$

where $V_2(r_i)$ describes the interaction of the electron with the core of charge Q, and the quantities ℓ_2 and R are given in equation (2.7) in terms of the second ionisation energy $-E_2$ of the alkaline earth sequence.

To develop a simple, compact, but accurate wave function of the two electron state, we note some properties of the wave function. We first note that since the potential has an infinite barrier for $r < R$, the wave function vanishes for $r_i < R$:

$$\psi(\mathbf{R}, \mathbf{r}_2) = \psi(\mathbf{r}_1, \mathbf{R}) = 0. \tag{3.2}$$

Particularly important are the properties of the wave function in the asymptotic region when one of the electrons is far away, or the two electrons are close to each other.

Asymptotic behaviour

It has been shown [13,14] that when one of the electrons is far away,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) \overset{r_1 \rightarrow \infty}{\longrightarrow} \phi_2(\mathbf{r}_2)\eta_1(\mathbf{r}_1) \tag{3.3}$$

where $\phi_2(r_2)$ is the ground state wave function of the remaining electron and

$$\begin{aligned} \eta_1(\mathbf{r}_1) &= r_1^{u_1}[1 + c_1/r_1 + ...]\mathrm{e}^{-a_1 r_1} \\ a_1 &= (-2E_1)^{1/2} \\ u_1 &= \frac{Q-1}{a_1} - 1 \\ c_1 &= \frac{(\ell_0 - u_1)(\ell_0 + u_1 + 1)}{2a_1} \end{aligned} \tag{3.4}$$

with $-E_1$ being the ionisation energy of the atom or ion and $Q - 1$ being the charge seen by the electron 1 when it is far away. The coefficient c_1 is related to the coefficient $\ell_0(\ell_0 + 1)/2$ of the $1/r^2$ term in the radial equation. The value of ℓ_0 in the present case is obtained from the equation

$$\ell_0(\ell_0 + 1) = \ell(\ell + 1) + \ell_2(\ell_2 + 1) \tag{3.5}$$

where ℓ is the orbital angular momentum quantum number of the outer electron. We have a similar relation when electron 2 is far away.

Cusp condition

When the two electrons are close to each other, the $1/r_{12}$ singularity in the potential has to be canceled by the kinetic energy term for the regular solution. This implies for $r_{12} \rightarrow 0$,

$$\begin{aligned} \psi(\mathbf{r}_1, \mathbf{r}_2) &\rightarrow b_0(1 + \frac{1}{2}r_{12}) \qquad \text{for the singlet} \\ &\rightarrow b_0 r_{12}(1 + \frac{1}{4}r_{12}) \quad \text{for the triplet} \end{aligned} \tag{3.6}$$

which are known as the cusp conditions [15]. They have been found to play an important role [10,11] in the development of reliable wave functions for two-electron systems.

Wave function for the ground state

We propose a simple, ground-state wave function for the outer electrons in the alkaline earth sequences, which incorporates these general properties,

$$\begin{aligned} \psi(\mathbf{r}_1, \mathbf{r}_2) &= N[\phi_1(r_1)\phi_2(r_2) + \phi_2(r_1)\phi_1(r_2)]f_1(r_{12}) \\ &= 0 \quad \text{for} \quad r_i < R, \\ \phi_1(r) &= (r - R)(r + d)^{u_1 - 2}\mathrm{e}^{-a_1 r} \\ \phi_2(r) &= (r - R)r^{\ell_2}\mathrm{e}^{-a_2 r} \\ f_1(r_{12}) &= 1 + \frac{1}{2}r_{12} \end{aligned} \tag{3.7}$$

where a_1 and u_1 are related to the ionisation energy $-E_1$ as in equation (3.4) and ℓ_2,a_2 and R are related to the second ionisation energy $-E_2$ (ionisation energy of the remaining electron after the first electron has been removed) as in equation (2.7), and d is a variational parameter. This wave function vanishes at $r_i = R$, has the correct leading asymptotic behaviour (note that $r_{12} \rightarrow r_i$ for $r_i \rightarrow \infty$), and has the correct singlet cusp condition for $r_{12} \rightarrow 0$. It can be used to calculate the two-electron energy

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \tag{3.8}$$

where the Hamiltonian H is given in equation (3.1). The parameters u_1 and a_1 which depend on the first ionisation energy $-E_1$ are determined iteratively by using

$$E_1 = E - E_2. \tag{3.9}$$

The only input parameter is the second ionisation energy $-E_2$ which ensures that the electrons singly interact correctly with the core. The variational parameter d is determined by minimising the energy.

The calculations of the average kinetic energy are simplified by the use of the identity [8]

$$\int(\phi f)\nabla^2(\phi f)\mathrm{d}\tau = \int[f^2\phi\nabla^2\phi - \phi^2(\boldsymbol{\nabla} f)\cdot(\boldsymbol{\nabla} f)]\mathrm{d}\tau \tag{3.10}$$

which follows from simplifying the left-hand-side and integrating by parts. The calculated values of the total energy, along with the normalization constant, and the expectation values of $\langle\sum_i r_i^2\rangle$ and $\langle\sum_i r_i^4\rangle$ are given in Table 1. Our values of E agree with the experimental values [16] to within 1.0% for all the 14 members of the alkaline earth isoelectronic sequences. This suggests that our model potential in equation (3.1) and the model wave function in equation (3.7) are quite reliable. Our values for $\langle\sum_i r_i^2\rangle$ for Be, Mg, and Ca are 16.08, 22.93, and 35.22 which are in good agreement with the values of 15.83, 23.35, and 35.92 respectively obtained by Maeder and Kutzelnigg [12]. There do not appear to be reliable values for other systems we have considered. Our predictions for the negative ions are new. Since our wave functions incorporate

Table 1. Input values of the second ionisation energy $-E_2$, variational value of parameter d, predicted and experimental values of total energy E ($-E$ is the sum of the first and second ionisation energies), $\langle \sum_i r_i^2 \rangle$, $\langle \sum_i r_i^4 \rangle$ along with the normalization constant N, for the outer two electrons in the ground state of the alkaline earth sequences.

	$-E_2$ (eV)	d	N	$-E$	$-E_{\text{expt}}$	$\langle r^2 \rangle$	$\langle r^4 \rangle$
Be	18.2112	1.68	0.6117	1.0122	1.0118	16.08	227.2
Mg	15.0353	2.20	0.4101	0.8386	0.8335	22.93	441.1
Ca	11.8717	3.35	0.2340	0.6643	0.6609	35.22	986.5
Sr	11.0301	3.90	0.1902	0.6178	0.6146	40.28	1270
Ba	10.0039	4.90	0.1445	0.5609	0.5592	48.05	1771
B^+	37.931	1.45	1.666	2.316	2.318	7.668	49.6
Al^+	28.448	2.40	2.783	1.742	1.737	13.07	135.4
C^{++}	64.494	1.34	5.769	4.124	4.130	4.51	16.9
Si^{++}	45.142	3.00	9.2617	2.893	2.890	8.80	59.5
Li^-	5.3917	3.30	0.2672	0.2214	0.2209	68.9	5562
Na^-	5.1391	3.30	0.2310	0.2114	0.2090	75.6	6728
K^-	4.3407	4.30	0.2259	0.1794	0.1779	100.0	1.09×10^4
Rb^-	4.1771	4.50	0.2182	0.1728	0.1714	106.5	1.22×10^4
Cs^-	3.8939	5.10	0.2184	0.1613	0.1604	119.6	1.49×10^4

the correct asymptotic behaviour, we expect these predictions to be quite reliable. It may be mentioned that since $\langle \sum r_i^{2n} \rangle$ are sensitive to the asymptotic behaviour of the wave function, they are calculated with the wave functions satisfying the correct asymptotic behaviour in terms of the experimental ionisation energies, though our calculated values of the energies are close to the experimental values.

Wave function for the triplet ^{3}S state

We also consider the wave function for the lowest energy, triplet ^3S states of the alkaline earth sequences. For this state we propose a wave function

$$\begin{aligned} \psi(\mathbf{r}_1, \mathbf{r}_2) &= A[\phi_3(r_1)\phi_2(r_2) - \phi_2(r_1)\phi_3(r_2)] f_3(r_{12}) \\ &= 0 \quad \text{for} \quad r_i < R, \\ \phi_2(r) &= (r - R) r^{\ell_2} \mathrm{e}^{-a_2 r} \\ \phi_3(r) &= (r - R)(1 + c_3/r) r^{u_3 - 1} \mathrm{e}^{-a_3 r} \end{aligned} \tag{3.11}$$

where a_2, ℓ_2 and R are related to the second ionisation energy $-E_2$ as in equation (2.7) and a_3 and u_3 are related to the ionisation energy $-E_3$ of the triplet state as

$$a_3 = (-2E_3)^{1/2}, \quad u_3 = \frac{Q-1}{a_3} - 1. \tag{3.12}$$

Since one of the electrons in the triplet state is in an excited state, we impose the asymptotic behaviour for both the leading terms in equation (3.4), which implies that the c_3 in equation (3.11) is given by

$$c_3 = R + \frac{(\ell_2 - u_3)(\ell_2 + u_3 + 1)}{2a_3} \tag{3.13}$$

with ℓ_2 given in equation (2.7). For the correlation function $f_3(r_{12})$ we take

$$f_3(r_{12}) = 1 - \frac{1}{1 + 4\lambda} \mathrm{e}^{-\lambda r_{12}} \tag{3.14}$$

which has the correct, triplet cusp condition in equation (3.6) for $r_{12} \to 0$, and we take λ to be a variational parameter. The wave function in equation (3.11) vanishes at $r_i = R$, has the correct asymptotic behaviour, and has the correct cusp condition for $r_{12} \to 0$. We use it for calculating the energy as in equation (3.8). The quantities u_3 and a_3 depend on the ionisation energy $-E_3$ of the triplet state, and are determined iteratively by using

$$E_3 = E - E_2. \tag{3.15}$$

The calculations are again simplified by the use of the identity in equation (3.10). The calculated values of the total energy, along with the normalization constant A, and the expectation values of $\langle \sum r_i^2 \rangle$, $\langle \sum r_i^4 \rangle$ are given in Table 2. Our values of E agree with the experimental values [16,17] to within 1% for all the members of the alkaline earth sequences we have considered.

4 Multipolar polarisabilities and hyperpolarisabilities

Our wave function in equation (3.7) can be used to calculate multipolar polarisabilities and hyperpolarisabilities of the sequences. In the presence of a perturbative multipolar potential, the perturbation to the wave function, $\delta\psi_\ell$, satisfies the inhomogeneous equation

$$(H - E)\delta\psi_\ell = [r_1^\ell P_\ell(\cos\theta_1) + r_2^\ell P_\ell(\cos\theta_2)]\psi \tag{4.1}$$

where H is the unperturbed Hamiltonian given in equation (3.1), and ψ is the unperturbed ground-state wave function given in equation (3.7). The multipolar polarisability α_ℓ is given by

$$\alpha_\ell = 2\langle \psi | [r_1^\ell P_\ell(\cos\theta_1) + r_2^\ell P_\ell(\cos\theta_2)] | \delta\psi_\ell \rangle. \tag{4.2}$$

Table 2. Variational values of the parameter λ, predicted and experimental values of the energy E ($-E$ is the total separation energy of the two electrons in the triplet state), $\langle\sum_i r_i^2\rangle$, $\langle\sum_i r_i^4\rangle$ along with the normalization constant A, for the outer two electrons in the lowest energy ${}^3S$ state of the alkaline earth sequences.

	λ	A	$-E$	$-E_{\text{expt}}$	$\langle r^2\rangle$	$\langle r^4\rangle$
Be	0.12	0.0358	0.7730	0.7745	78.3	7.75×10^3
Mg	0.08	0.0318	0.6452	0.6458	100	1.22×10^4
Ca	0.04	0.0271	0.5165	0.5172	137	2.18×10^4
Sr	0.03	0.0263	0.4820	0.4823	152	2.63×10^4
Ba	0.02	0.0260	0.4397	0.4400	172	3.30×10^4
B^+	0.20	0.232	1.722	1.727	30.5	1.09×10^3
Al^+	0.10	0.203	1.318	1.321	45.6	2.29×10^3
C^{++}	0.30	0.893	3.033	3.045	16.5	308
Si^{++}	0.20	0.638	2.181	2.192	27.0	757

For solving equation (4.1) variationally, we note that

$$\begin{aligned} G = {} & \langle\delta\psi_\ell|(H-E)|\delta\psi_\ell\rangle \\ & - 2\langle\psi|[r_1^\ell P_\ell(\cos\theta_1) + r_2^\ell P_\ell(\cos\theta_2)]|\delta\psi_\ell\rangle \end{aligned} \tag{4.3}$$

is an extremum for the solutions of equation (4.1). We also observe that the solution to equation (4.1) has an asymptotic behaviour

$$\delta\psi_\ell \overset{r_1\to\infty}{\longrightarrow} r_1^{\ell+u_1+1} P_\ell(\cos\theta_1) \mathrm{e}^{-a_1 r_1} \phi_2(r_2) \tag{4.4}$$

where a_1 and u_1 are given in equation (3.4) and $\phi_2(r_2)$ given in equation (3.7) is the ground-state wave function of the remaining electron. We therefore take

$$\begin{aligned} & \delta\psi_\ell = C_\ell \eta_\ell(\mathbf{r}_1, \mathbf{r}_2) \\ & \eta_\ell(\mathbf{r}_1, \mathbf{r}_2) = [(r_1 - R) r_1^{\ell+u_1-1} P_\ell(\cos\theta_1) \mathrm{e}^{-a_1 r_1} \phi_2(r_2) \\ & \qquad + (r_2 - R) r_2^{\ell+u_1-1} P_\ell(\cos\theta_2) \mathrm{e}^{-a_1 r_2} \phi_2(r_1)] f(r_{12}) \end{aligned} \tag{4.5}$$

where C_ℓ is a variational parameter, and a_1 and u_1 are given in equation (3.4). Extremising G in equation (4.3), leads to

$$C_\ell = \frac{\langle\psi|[r_1^\ell P_\ell(\cos\theta_1) + r_2^\ell P_\ell(\cos\theta_2)]|\eta_\ell\rangle}{\langle\eta_\ell|(H-E)|\eta_\ell\rangle} \tag{4.6}$$

and

$$\alpha_\ell = 2\frac{[\langle\psi|[r_1^\ell P_\ell(\cos\theta_1) + r_2^\ell P_\ell(\cos\theta_2)]|\eta_\ell\rangle]^2}{\langle\eta_\ell|(H-E)|\eta_\ell\rangle}\cdot \tag{4.7}$$

Once again we use the identity in equation (3.10) to simplify the evaluation of the expectation value of the kinetic energy in equations (4.6, 4.7). We also note the relation

$$\int P_\ell(\cos\theta_1) P_\ell(\cos\theta_2) F(r_{12}) \mathrm{d}\Omega_1 \mathrm{d}\Omega_2 = \frac{4\pi}{2\ell+1}\int P_\ell(\cos\theta_{12}) F(r_{12}) \mathrm{d}\Omega_{12} \tag{4.8}$$

which simplifies the angular integrations. The calculated values of the variational parameters C_1 and C_2, and the polarisabilities α_ℓ are given in Table 3. It may be noted that since the asymptotic behaviour is of considerable importance in the evaluation of the polarisabilities, we have used the experimental values of the two-electron energies though there is very little difference between the experimental values and our calculated values (Tab. 1). Our values of α_1 for Be, Mg, Ca are 37.9, 72.0, and 152.7 which are in good agreement with the values of 36.7, 70.5, 153.7 respectively obtained by Maeder and Kutzelnigg [12]. Our values for some of the other systems, particularly the negative ions, are new.

The wave functions $\delta\psi_\ell$ in equation (4.5) can be used for calculating hyperpolarisability B defined as

$$B = -2T_{121} - 4T_{112} \tag{4.9}$$

where

$$T_{121} = \langle\delta\psi_1|[r_1^2 P_2(\cos\theta_1) + r_2^2 P_2(\cos\theta_2)]|\delta\psi_1\rangle \tag{4.10}$$

$$T_{112} = \langle\delta\psi_1|[r_1 P_1(\cos\theta_1) + r_2 P_1(\cos\theta_2)]|\delta\psi_2\rangle. \tag{4.11}$$

We again note that the angular integrations are simplified by the relations

$$\int P_1(\cos\theta_1) P_1(\cos\theta_1) P_2(\cos\theta_2) F(r_{12}) \mathrm{d}\Omega_1 \mathrm{d}\Omega_2 = \frac{8\pi}{15}\int P_2(\cos\theta_{12}) F(r_{12}) \mathrm{d}\Omega_{12} \tag{4.12}$$

and

$$\int P_1(\cos\theta_1) P_1(\cos\theta_2) P_2(\cos\theta_2) F(r_{12}) \mathrm{d}\Omega_1 \mathrm{d}\Omega_2 = \frac{8\pi}{15}\int P_1(\cos\theta_{12}) F(r_{12}) \mathrm{d}\Omega_{12}. \tag{4.13}$$

The predicted values of B are given in Table 3. The only previous calculations of B available for comparison are the ones for Be. The calculation of Bhattacharya and Mukherjee [18] based on CHF gave a value of -3343 whereas Maroulis and Thakkar [19] obtained a value of -2140. Our value of -2860 is close to the average of the two. Since our analysis incorporates the correct asymptotic behaviour and correlation, we expect our predictions to be correct to within 10–15%.

5 Dispersion coefficients

We can calculate the dispersion coefficients for alkaline earth atoms by using their representation in terms of dynamic polarisabilities

$$C_{2n}(AB) = \frac{(2n-2)!}{2\pi}\sum_{\ell=1}^{n-2}\frac{1}{(2\ell)!(2\ell')!} \times \int_0^\infty \alpha_\ell^A(\mathrm{i}\omega)\alpha_{\ell'}^B(\mathrm{i}\omega)\mathrm{d}\omega \tag{5.1}$$

Table 3. Values of the variational parameters C_1, C_2, predicted values of multipolar polarisabilities α_1, α_2, α_3, and of hyperpolarisability B.

	C_1	C_2	α_1	α_2	α_3	$-B$
Be	0.702	0.425	37.9	271	3488	2.86×10^3
Mg	0.536	0.325	72.0	709	1.17×10^4	9.79×10^3
Ca	0.335	0.208	152.7	2248	5.08×10^4	4.06×10^4
Sr	0.278	0.174	193.2	3237	8.07×10^4	6.36×10^4
Ba	0.212	0.135	261.2	5204	1.48×10^5	1.12×10^5
B^+	2.31	1.32	8.87	26.1	146	124
Al^+	1.66	0.953	23.3	112	919	792
C^{++}	5.86	3.25	3.19	5.06	15.9	14.2
Si^{++}	4.37	2.41	10.7	31.2	161	146
Li^-	0.353	0.273	780	4.55×10^4	5.59×10^6	2.77×10^6
Na^-	0.340	0.258	966	6.21×10^4	8.54×10^6	4.43×10^6
K^-	0.311	0.245	1478	1.17×10^5	1.81×10^7	8.81×10^6
Rb^-	0.301	0.239	1638	1.36×10^5	2.17×10^7	1.06×10^7
Cs^-	0.285	0.231	1939	1.77×10^5	2.95×10^7	1.37×10^7

with $\ell' = n - \ell - 1$, where $\alpha_\ell^A(\mathrm{i}\omega)$ and $\alpha_{\ell'}^B(\mathrm{i}\omega)$ are the dynamic polarisabilities of the atoms,

$$\alpha_\ell(\mathrm{i}\omega) = 2\sum_j \frac{|\langle j|\sum_i r_i^\ell P_\ell(\cos\theta_i)|0\rangle|^2 (E_j - E_0)}{(E_j - E_0)^2 + \omega^2}\cdot \qquad (5.2)$$

For large values of ω, $\alpha_\ell(\mathrm{i}\omega)$ has the limiting behaviour

$$\alpha_\ell(\mathrm{i}\omega) \to \beta_\ell/\omega^2, \quad \text{for} \quad \omega \to \infty \qquad (5.3)$$

with

$$\begin{aligned}\beta_\ell &= 2\sum_j |\langle j|\sum_i r_i^\ell P_\ell(\cos\theta_i)|0\rangle|^2 (E_j - E_0)\\ &= \ell\langle 0|\sum_i r_i^{2\ell-2}|0\rangle. \end{aligned} \qquad (5.4)$$

We therefore consider a parametric representation

$$\alpha_\ell(\mathrm{i}\omega) = \frac{\beta_\ell}{\omega^2 + \beta_\ell/\alpha_\ell} \qquad (5.5)$$

with β_ℓ given in equation (5.4), which has the correct limiting value for $\omega \to 0$ and $\omega \to \infty$. Using this in equation (5.1), we get

$$\begin{aligned} C_{2n}(AB) &= \frac{(2n-2)!}{2\pi} \\ &\times \sum_{\ell=1}^{n-2} \frac{1}{(2\ell)!(2\ell')!} \frac{\alpha_\ell^A \alpha_{\ell'}^B}{(\alpha_\ell^A/\beta_\ell^A)^{1/2} + (\alpha_{\ell'}^B/\beta_{\ell'}^B)^{1/2}} \end{aligned} \qquad (5.6)$$

with $\ell' = n - \ell - 1$. In the present case

$$\beta_1 = 2, \quad \beta_2 = 2\left\langle \sum_i r_i^2 \right\rangle, \quad \beta_3 = 3\left\langle \sum_i r_i^4 \right\rangle. \qquad (5.7)$$

Table 4. Calculated values of C_6, C_8, and C_{10} obtained from equation (5.6).

	C_6	C_8	C_{10}
Be–Be	248	1.06×10^4	5.01×10^5
Be–Mg	396	2.04×10^4	1.13×10^6
Be–Ca	663	4.53×10^4	3.17×10^6
Be–Sr	775	5.85×10^4	4.44×10^6
Be–Ba	941	8.17×10^4	6.95×10^6
Mg–Mg	648	3.85×10^4	2.43×10^6
Mg–Ca	1119	8.41×10^4	6.50×10^6
Mg–Sr	1319	1.08×10^5	8.98×10^6
Mg–Ba	1619	1.50×10^5	1.38×10^7
Ca–Ca	2002	1.79×10^5	1.63×10^7
Ca–Sr	2384	2.28×10^5	2.20×10^7
Ca–Ba	2967	3.14×10^5	3.30×10^7
Sr–Sr	2849	2.90×10^5	2.96×10^7
Sr–Ba	3562	3.98×10^5	4.40×10^7
Ba–Ba	4479	5.43×10^5	6.46×10^7

Using the values of α_ℓ and $\langle\sum_i r_i^{2n}\rangle$ we have obtained, we deduce the dispersion coefficients C_6, C_8, and C_{10}. The calculated values of C_6, C_8, and C_{10} are given in Table 4. Our values for Be, Mg, and Ca are in agreement with the values of Maeder and Kutzelnigg[12] generally to within 10–15%.

6 Conclusions

We have developed a simple model potential with an infinite potential barrier for small r, and the correct

Coulombic behaviour for large r, to describe the interaction of an electron with a closed-shell core. This potential has a simple, exact analytic expression for the ground state wave function, with the correct experimental energy. This potential is able to predict the two-electron energies of 14 members of the alkaline earth isoelectronic sequences including negative ions, and the triplet state energies of some members, to within 1% accuracy. We have used the potential and the wave functions to analyse the perturbations due to multipolar potentials, and to calculate the multipolar polarisabilities and hyperpolarisabilities of the sequences. We have also calculated the dispersion coefficients using the polarisabilities and the expectation values $\langle \sum_i r_i^{2n} \rangle$. Our calculated values are generally in good agreement with the results from other calculations. For many systems, our results are new and should be of considerable use in the analysis of the interaction of alkaline earth sequences with each other and with external fields.

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