International Journal of Scientific Research and Management (IJSRM)
||Volume||5||Issue||07||Pages||6165-6172||2017||
Website: www.ijsrm.in ISSN (e): 2321-3418
Index Copernicus value (2015): 57.47 DOI: 10.18535/ijsrm/v5i7.44

Electronic Structure Problem of Alkaline Earth Metals

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Abstract

Purpose: The present study is to resolve the problem in electronic structure of alkaline earth metals bydifferent calculations and conceptual theories.

Methodological concept: All discovered alkaline earth metals occur in nature. Experiments have beenconducted to attempt the synthesis of element 120, the next potential member of the group, but they have allmet with failure. The electronic structure of alkaline earth metals determines all their physical properties.Effective electron Eigen value problem of the singly charged alkaline earth metal ion with a single valenceelectron. This valence electron moves in one particle model potential to reproduce the valence excitationenergies of the monocation.

Results: The radial degree of freedom of the electronic wave function in a finite element basis set from thesolution of the one electron problem. Using the Lanczos-based package ARPACK, we calculate-for eachvalid combination of angular momentum quantum numbers l and j-the first 18 eigen functions outside thecore shells. In other words, solutions associated with inner shells are skipped. Thus, the selected valence-electron solutions display correct nodal behavior.

Keywords: Alkaline earth metals, electronic structure, valence electrons.

1. Introduction

The alkaline earth metals are six chemical elements in column (Group) 2 of the Periodic table. They are beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba), and Radium (Ra). They have very similar properties: they are all shiny, silvery-white, somewhat reactive metals at standard temperature and pressure. Structurally, they have in common an outer s- electron shell which is full; that is, this orbital contains its full complement of two electrons, which these elements readily lose to form cations with charge +2, and an oxidation state (oxidation number) of +2 [1-8]. All the discovered alkaline earth metals occur in nature. Experiments have been conducted to attempt the synthesis of element 120, the next potential member of the group, but they have all met with failure. The electronic structure of alkaline earth atoms determines all their physical properties. Effective electron eigen value problem of the singly charged alkaline earth metal ion with a single valence electron. This valence electron moves in one particle model potential to reproduce the valence excitation energies of the monocation. We represent the radial degree of freedom of the electronic wave function in a finite element basis set from the solution of the one electron problem. Two electron basis functions are constructed. The effective two electrons Hamiltonian which describes the neutral atoms and which fully incorporates valence electron correlation is represented in this basis diagnolized [9-16].

2. Calculations

A. One-particle Hamiltonian

When treating the effective one-electron problem of the monocation, we employ the one-electron Hamiltonian

$$h_1 = -\frac{1}{2}\nabla^2 + V + V^{(\mathrm{so})}.$$

The operator V represents the electrostatic field generated by the noble-gas like core. This is a central field. However, an explicit dependence of the associated potential on the orbital angular momentum quantum number l must be included to take account of the fact that electrons with l = 0 dive deep into the core and experience relativistic effects (orbital contraction). Such scalar relativistic effects decrease with the average distance from the nucleus and thus with l. Therefore, we assume that the spin-angular representation of V can be written as

$$\langle j, m_j, l, s|\, V \,|j', m_{j'}, l', s\rangle = \delta_{j,j'}\delta_{m_j,m_{j'}}\delta_{l,l'}V_l(r).$$

The quantum numbers j and m_j refer to the total angular momentum of the valence electron, s = 1/2 denotes its spin. In this work, the following parameterization of $V_l(r)$ is used:

$$\begin{aligned} V_l(r) = {} & -\frac{1}{r}\{2 + (Z-2)\exp(-\alpha_{l,1},r) + \alpha_{l,2} r exp(-\alpha_{l,3} r)\} \\ & -\frac{\alpha_{cp}}{2r^4}\left\{1 - \exp\left[-\left(\frac{r}{rl}\right)^6\right]\right\}. \end{aligned}$$

Z is the nuclear charge. The parameters $\alpha_{l,1}, \alpha_{l,2}, \alpha_{l,3}, \alpha_{cp}$ and r_l are listed. The potential $V_l(r)$ describes the interaction of the valence electron with the ionic core at various length scales. For very large distances from the core, the electron is attracted by a point charge of charge +2. As the electron comes closer, the ionic core responds to the presence of the electron and becomes polarized, as expressed by the term proportional to cp/r4. Below r = r_l, the electron dives into the core. The parameters $\alpha_{l,1}, \alpha_{l,2}, and\ \alpha_{l,3}$ mediate the transition from the exterior region of the core to the interior, where at very small length scales the electron interacts with the unscreened charge Z.

Spin-orbit interaction is represented in Eq. (1) by the operator $V^{(so)}$:

$$\langle j, m_j, l, s| V^{(\mathrm{so})} |j', m_{j'}, l', s\rangle = \delta_{j,j'}\delta_{m_j,m_{j'}}\delta_{l,l'}V_{l,j}^{(\mathrm{so})}(r),$$

where,

$$\begin{aligned} V_{l,j}^{(\mathrm{so})}(r) &= \{j(j+1) - l(l+1) - s(s+1)\} \\ &\quad \times \frac{\alpha^2}{4r}\frac{\mathrm{d}V_l}{\mathrm{d}r}\left[1 - \frac{\alpha^2}{2}V_l\right]^{-2}, \end{aligned}$$

and $\alpha \approx 1/137.036$ is the fine-structure constant.

The Eigen states of h_1 can now be written as

$$\psi = \frac{u_{l,j}(r)}{r}\left|j, m_j, l, s\right\rangle,$$

and we can focus on solving the radial equation,

$$\bar{h}_{l,j}u_{l,j}(r) = \varepsilon_{l,j}u_{l,j}(r), \quad u_{l,j}(0) = 0,$$

$$\bar{h}_{l,j} = -\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_l(r) + V_{l,j}^{(\mathrm{so})}(r).$$

To this end, we apply a technique based on finite elements.

B. Finite-element basis

For the radial degree of freedom, we introduce a quadratically spaced grid of N + 1 grid points between r = 0 and r = r_{max}, i.e., $r_i = r_{max}i^2/N^2$, i = 0, ...,N. In each interval [r_i, r_{i+1}], six unique, linearly independent fifth-order Hermite interpolating polynomials can be constructed that satisfy the boundary conditions [17-24].

$$\left.\frac{d^k P_{j,i}(r)}{dr^k}\right|_{r=r_i} = \delta_{j,k},$$

$$\left.\frac{d^k P_{j,i}(r)}{dr^k}\right|_{r=r_{i+1}} = 0,$$

$$\left.\frac{d^k Q_{j,i}(r)}{dr^k}\right|_{r=r_{i+1}} = \delta_{j,k},$$

$$\left.\frac{d^k Q_{j,i}(r)}{dr^k}\right|_{r=r_i} = 0,$$

Where j, k = 0, 1, 2. The functions are defined to vanish everywhere outside $[r_i, r_{i+1}]$. Using the definitions

$$\begin{aligned} g_0(r) &= f(r)^3\left[6f(r)^2 - 15f(r) + 10\right], \\ g_1(r) &= \Delta r f(r)^3\left[3f(r)^2 - 7f(r) + 4\right], \\ g_2(r) &= \frac{1}{2}\Delta r^2 f(r)^3\left[f(r) - 1\right]^2, \end{aligned}$$

we have, for $r \in [r_i, r_{i+1}]$ and j = 0, 1, 2,

$$P_{j,i}(r) = g_j(r),\ \ \Delta r = r_{i+1} - r_i,\ \ f(r) = -\frac{r - r_{i+1}}{\Delta r}$$

And

$$Q_{j,i}(r) = g_j(r),\ \ \Delta r = r_i - r_{i+1},\ \ f(r) = -\frac{r - r_i}{\Delta r}.$$

These formulas correct some misprints in equation. Three continuous basis functions, with continuous first and second derivatives, can now be associated with grid point r_i ($i = 1, \ldots, N - 1$):

$$B_{j,i}(r) = P_{j,i}(r) + Q_{j,i-1}(r),\ \ j = 0, 1, 2.$$

Using these, the function value at grid point r_i, the first derivative, and the second derivative of any wave function can be represented. At the end points, r_0 and r_N, we set

$$B_{0,0}(r) = 0,\ \ B_{j,0}(r) = P_{j,0}(r),\ \ j = 1, 2,$$

which is consistent with the boundary condition specified in equation, and

$$B_{0,N}(r) = 0, \;\; B_{j,N}(r) = Q_{j,N-1}(r), \;\; j = 1, 2,$$

which selects solutions to Eq. (7) that vanish at r = r_{max}.

The solutions to the Eigen value problem of $\bar{h}$,

$$\bar{h} u_k(r) = \varepsilon_k u_k(r),$$

(the explicit dependence on angular momentum quantum numbers is suppressed) are found by expanding the eigen-functions in terms of the finite-element basis functions $B_{j,i}(r)$:

$$uk(r) = \sum_{i=0}^{N} \sum_{j=0}^{2} \beta_{(j,i),k} B_{j,i}(r).$$

Hence, we have to solve the generalized Eigen value problem

$$\bar{h}\beta_k = \varepsilon_k o \beta_k,$$

Where,

$$(\bar{h})_{(j,i),(j',i')} = \int_0^{t_{max}} dr B_{j,i}\,(r) \bar{h} B_{J'I'}(r),$$

$$(O)_{(j,i),(j',i')} = \int_0^{t_{max}} dr B_{j,i}\,(r) B_{J'I'}(r),$$

and

$$(\beta_k)_{(j,i)} = \beta_{(j,i),k}$$

3. Results and discussion

In this present work our strategy toward solving the electronic structure problem of alkaline earth metal atoms we first treat the effective one electron Eigen value problem of the singly charged alkaline earth metal ion with single valence electron from the solution of the one electron problem of monocation we employ the one electron Hamiltonian .

$$h_1 = -\frac{1}{2}\nabla^2 + V + V^{(\mathrm{so})}.$$

The operator v represent the electronic field generated by th noble gas like core.For the radial degree of freedom, we introduce the degree of freedom, we introduce quadratic ally spaced grid of N+1 grid points between r=0 and r= r_{max}

i.e. $r_i = r_{max}\, i^2/N^2$, i=0,1,2,3……………..,N.

The effective two electron Hamiltonian which describes the neutral atom and which fully incorporated valence electron correlation is represented in this basis and diagonal zed in this way Eigen energies and Eigen vectors of the two electron valence shell are obtained.

4. Conclusion

Since the basis function $B_{j,i}(r)$ vanishes outside $[r_{i-1}, r_{i+1}]$, both matrices, $\bar{h}$ and o, have a simple banded structure with small bandwidth. The high degree of sparsity is ideal for iterative solvers. Using the Lanczos-based package ARPACK, we calculate-for each valid combination of angular momentum quantum numbers l and j-the first 18 Eigen functions outside the core shells. In other words, solutions associated with inner shells are skipped. Thus, the selected valence-electron solutions display correct nodal behavior.

5. References

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