

Evaluation of Core Correlation Effects in the $4s4p\ ^1P^0$ State of Calcium

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Abstract

In this paper two different approaches are used to study core correlation effects in the $3p^64s4p\ ^1P^0$ state of calcium. We show that the number of relevant configurational functions in the configuration interaction expansion can be reduced by determining the core correlation functions prior to the valence correlation functions. We also show that core correlation effects of the form $3p^2 \rightarrow nl^2$ can be represented in the configuration interaction expansion by including configurational functions of the type $3p^4(^S L)nl^2(^S L)\{^1S\}4s4p$ in the expansion.

1. Introduction

The study of correlation effects in atoms and ions has received much attention from theoreticians. The aim has been to develop a theory for the accurate calculation of energy separations, transition energies, transition probabilities and atomic polarizabilities. In general, quite accurate results can be obtained by using a fixed core approximation and carrying out a detailed study of the valence correlation effects. However, for some atomic systems, core-valence and core correlation effects are also important.

The approach most commonly used to study valence, core-valence and core correlation effects is:

- (i) to determine correlation functions to describe the valence correlation effect;
- (ii) additional correlations are then determined to describe the core correlation effect.

An alternative approach is:

- (i) to determine correlation functions to describe the core correlation effect;
- (ii) additional correlation functions are then determined to describe the valence correlation effect.

In this paper we look at the feasibility of both methods using the $4s4p\ ^1P^0$ state of calcium as an example, as a result of the large $4s \rightarrow nl$ and $3p^2 \rightarrow nd^2$ valence and core correlation effects respectively.

2. Radial Functions

The radial functions used in the calculations are determined in a LS coupled representation of the atomic states. The atomic state wavefunctions are represented by the configuration interaction expansion

$$\Psi(LS) = \sum_{i=1}^N c_i \Phi_i(\alpha_i; LS), \quad (1)$$

where the $\{\Phi_i\}$ are single configurational functions constructed from the one-electron (spin) orbitals

$$u(r, m_s) = r^{-1} P_{nl}(r) Y_l^{m_l}(\theta, \phi) \chi(m_s), \quad (2)$$

and where L and S are the total orbital and spin angular momenta, and $\{\alpha_i\}$ specifies the angular momentum coupling scheme of the i th configuration. The radial functions $\{P_{nl}(r)\}$ are expanded in analytic form as

$$P_{nl}(r) = \sum_{j=1}^k C_{jnl} \phi_{jnl}(r), \quad (3)$$

where $k \geq n-l$, and where

$$\phi_{jnl}(r) = \{(2\xi_{jnl})^{2I_{jnl}+1}/(2I_{jnl})!\}^{\frac{1}{2}} r^{I_{jnl}} \exp(-\xi_{jnl} r). \quad (4)$$

We also require the radial functions, for a given value of l , to form an orthonormal set:

$$\int_0^\infty P_{nl}(r) P_{n'l}(r) dr = \delta_{nn'}; \quad l+1 \leq n' \leq n. \quad (5)$$

If $k = n-l$ then the coefficients $\{C_{jnl}\}$ are uniquely determined by the orthonormality conditions, for a given choice of $\{I_{jnl}, \xi_{jnl}\}$. If $k > n-l$ some of the coefficients can be treated as variational parameters, either in Hartree-Fock calculations or in superposition of configurations calculations.

The coefficients $\{c_i\}$ in equation (1) are, for a given set of $\{\Phi_i\}$, the components of the appropriate eigenvector of the Hamiltonian matrix with elements

$$H_{ij} = \langle \Phi_i | \mathcal{H} | \Phi_j \rangle, \quad (6)$$

where \mathcal{H} represents the nonrelativistic Hamiltonian operator. The corresponding eigenvalue is given by

$$E = \langle \Psi(LS) | \mathcal{H} | \Psi(LS) \rangle, \quad (7)$$

where $\Psi(LS)$ is normalized to unity and E is, for the cases considered here, an upper bound to the corresponding exact energy (MacDonald 1933; Perkins 1965):

$$E \geq E_{\text{exact}}. \quad (8)$$

Different choices of the parameters C_{jnl} , I_{jnl} and ζ_{jnl} in equations (3) and (4), subject to the orthonormality condition in (5), will lead to different functions $\{\Phi_i\}$ and hence to different values of E and $\{c_i\}$.

Because of the upper bound property (8), it is possible to treat an eigenvalue as a variational function to be minimized with respect to $\{\zeta_{jnl}\}$ and those coefficients $\{C_{jnl}\}$ in (3) which are not determined by the orthonormality condition, *provided* configurations corresponding to lower lying states are included in the calculation. We have used the configuration interaction code CIV3 (Hibbert 1975; Glass and Hibbert 1978) in the *LS* coupling mode to determine the correlation radial functions $\{P_{nl}\}$.

Table 1. Contributions to correlation energy (in a.u.)

Excitation	Calculation A	Calculation B
4s \rightarrow 3d	0.01430	0.00000
4s \rightarrow 4d	0.00165	0.01450
3p ² \rightarrow 4d ²	0.12407	0.00000
3p ² \rightarrow 3d4d	0.00519	0.00000
3p ² \rightarrow 3d ²	0.00010	0.13071
Total correlation energy	0.14531	0.14520

3. Results and Discussion

The 1s, 2s, 2p, 3s, 3p, 4s Hartree-Fock radial functions were taken (Clementi and Roetti 1974) from the $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ S state of Ca II. The 4p radial function was taken from the $1s^2 2s^2 2p^6 3s^2 3p^6 4s 4p$ $^1P^0$ state optimizing on the $^1P^0$ eigenvalue of the single configuration wavefunction

$$3p^6 4s 4p. \quad (9)$$

Correlation functions were then determined as follows:

- (i) A 3d function was determined to describe the important $4s \rightarrow nd$ correlation effect. The exponents were optimized on the lowest $^1P^0$ eigenvalue of the two-configuration wavefunction

$$3p^6 4s 4p, \quad 3p^6 3d 4p. \quad (10)$$

- (ii) A 4d function was then determined to describe the $3p^2 \rightarrow nl^2$ core correlation effect. The exponents were optimized on the lowest $^1P^0$ eigenvalue of the five-configuration wavefunction

$$3p^6 4s 4p, \quad 3p^6 3d 4p, \quad 3p^4 ({}^3P) 4d^2 ({}^3P) \{ {}^1S \} 4s 4p, \\ 3p^4 ({}^1D) 4d^2 ({}^1D) \{ {}^1S \} 4s 4p, \quad 3p^4 ({}^1S) 4d^2 ({}^1S) \{ {}^1S \} 4s 4p. \quad (11)$$

Using the radial functions from Section 2 we performed a configuration interaction calculation including the configurations

$$3p^6 4s 4p, \quad 3p^6 3d 4p, \quad 3p^6 4d 4p, \quad 3p^4 3d^2 4s 4p, \quad 3p^4 3d 4d 4s 4p, \quad 3p^4 4d^2 4s 4p \quad (12)$$

in the wavefunction. In Table 1 (calculation A) the contribution to the correlation energy is given, each row representing the additional contribution to the correlation as a result of the new replacement up to and including that specified on the particular row. From an examination of the eigenvector composition for the $3p^6 4s 4p^1 P^0$ state it was found that the configurational functions with expansion coefficients greater than 10^{-3} in expansion (1) are

$$\begin{aligned} &3p^6 4s 4p, \quad 3p^6 3d 4p, \quad 3p^6 4d 4p, \quad 3p^4(^S L) 3d^2(^S L) \{^1 S\} 4s 4p, \\ &3p^4(^S L) 3d(^2 D) 4d \{^1 S\} 4s 4p, \quad 3p^4(^S L) 4d^2(^S L) \{^1 S\} 4s 4p, \end{aligned} \quad (13)$$

where

$$^S L = ^3 P, \quad ^1 D \text{ or } ^1 S. \quad (14)$$

Using the new set of configurational functions we recalculated the correlation energy for the $4s 4p^1 P^0$ state. The total correlation energy was found to be 0.1453 a.u., in excellent agreement with value given in Table 1. The number of configurational functions in expansion (1) has been reduced from 45 to 12. This is particularly important when studying correlation effects in the first-row transition metal atoms, where a detailed study of valence, core-valence and core correlation effects using the configuration interaction approach soon becomes unwieldy as a result of the large number of configurational functions needed in the expansion.

In the Introduction we mentioned that an alternative approach would be to study the core correlation effects first, followed by a study of the valence correlation effects. A new set of correlation functions was therefore found as follows:

- (i) A 3d function was determined to describe the important $3p^2 \rightarrow nd^2$ correlation effect. The exponents were optimized on the lowest $^1 P^0$ eigenvalue of the four-configuration wavefunction

$$\begin{aligned} &3p^6 4s 4p, \quad 3p^4(^3 P) 3d^2(^3 P) \{^1 S\} 4s 4p, \quad 3p^4(^1 D) 3d^2(^1 D) \{^1 S\} 4s 4p, \\ &3p^4(^1 S) 3d^2(^1 S) \{^1 S\} 4s 4p. \end{aligned} \quad (15)$$

- (ii) A 4d function was then determined to describe the $4s \rightarrow nd$ correlation effect. The exponents were optimized on the lowest $^1 P^0$ eigenvalue of the five-configuration wavefunction

$$\begin{aligned} &3p^6 4s 4p, \quad 3p^4(^3 P) 3d^2(^3 P) \{^1 S\} 4s 4p, \quad 3p^4(^1 D) 3d^2(^1 D) \{^1 S\} 4s 4p, \\ &3p^4(^1 S) 3d^2(^1 S) \{^1 S\} 4s 4p, \quad 3p^6 4d 4p. \end{aligned} \quad (16)$$

Using these configurations we performed a configuration interaction calculation including the configurations listed in (12) in the wavefunction. In Table 1 (calculation B) the contributions to the correlation energy from the various configurations are listed. Using this alternative approach we see that the only contributions to the correlation energy are from the $3p^2 \rightarrow 3d^2$ and $4s \rightarrow 4d$ replacements, the contributions from the replacements $4s \rightarrow 3d$, $3p^2 \rightarrow 3d 4d$ and $3p^2 \rightarrow 4d^2$ being negligible. This is in contrast to the results from the first approach, where the contributions to the correlation

energy from all replacements were significant. Also, from an examination of the eigenvector composition for the $3p^6 4s 4p \ ^1P^0$ state, it is found that the configurational functions with expansion coefficients greater than 10^{-3} in expansion (1) are

$$3p^6 4s 4p, \quad 3p^4(^5L)3d^2(^5L)\{^1S\}4s 4p, \quad 3p^6 4d 4p, \quad (17)$$

where the values for 5L are given in (14). The total correlation energy is 0.1452 a.u. in excellent agreement with the value given in Table 1 (calculation B). The number of configurational functions in expansion (1) has now been reduced to five.

In the variational approach radial functions are determined to minimize the energy of a particular functional expression with respect to variation in the radial functions. In the 'conventional' approach a 3d function is first determined to describe the valence $4s \rightarrow 4d$ correlation effect, the 3d function being optimized to minimize the energy of the lowest $^1P^0$ eigenvalue of the functional expression. However, there are large correlation effects arising from the $3p^2 \rightarrow nd^2$ replacements and the 3d function being minimized will capture some of the core correlation effect. The determination of the 4d function to describe the $3p^2 \rightarrow nd^2$ correlation will then capture the remaining correlation. In contrast, by using the 'alternative' approach, a 3d function is determined first to describe the core $3p^2 \rightarrow nd^2$ correlation effect. The 3d function being optimized to minimize the energy of the lowest $^1P^0$ eigenvalue of the functional expression will now capture *all* of the $3p^2 \rightarrow nd^2$ correlation. The determination of a 4d function to describe the valence $4s \rightarrow nd$ correlation will now only be optimized to capture the $4s \rightarrow nd$ correlation. That is, by using the 'conventional' approach, each electron excitation ($4s \rightarrow nd$, $3p^2 \rightarrow ndn'd$; $n \geq n'$) will contribute to the correlation energy, whereas only the electron excitations $3p^2 \rightarrow 3d^2$ and $4s \rightarrow 4d$ will contribute to the correlation energy in the alternative approach. Thus, the number of relevant configurational functions in the configuration interaction expansion can be reduced by determining the core correlation functions prior to the valence correlation functions.

The contribution to the correlation energy from the excitation $4s \rightarrow 3d 4p$ is negligible, even though the expansion coefficient of 0.03486 is quite sizeable. The configuration should however be included in the final configuration interaction expansion, because any configuration that does not contribute directly to the energy but has a sizeable expansion coefficient (≥ 0.01) may in fact still play an important role in the study of other atomic properties (Glass and Hibbert 1976).

4. Conclusions

In this paper we have used two different approaches to study core correlation effects in the $3p^6 4s 4p \ ^1P^0$ state of calcium. We have been able to show the following:

- (i) In the 'conventional' approach (where the valence correlation is evaluated first) each electron excitation ($4s \rightarrow nd$, $3p^2 \rightarrow ndn'd$; $n \geq n'$) contributes to the correlation energy and the number of relevant configurational functions in expansion (1) is given by (13).
- (ii) In the 'alternative' approach (where the core correlation is evaluated first) the only electron excitations that contribute to the correlation energy are $3p^2 \rightarrow 3d^2$ and $4s \rightarrow 4d$. The number of relevant configurational functions in expansion (1) is given by (17).

- (iii) For core correlation effects of the form $3p^2 \rightarrow nl^2$, the relevant configurational functions to be included in the configuration interaction expansion are $3p^4(^S L)nl^2(^S L)\{^1S\}4s4p$.

An important application of these results will be the investigation of correlation effects in the first-row transition metal atoms and ions, where a detailed study of valence, core-valence and core correlation effects using the conventional configuration interaction approach soon becomes unwieldy as a result of the large number of configurational functions in expansion (1).

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