PHYSICAL REVIEW A VOLUME 57, NUMBER 4 APRIL 1998

Calculation of the energy levels of barium using *B* splines and a combined configuration-interaction and many-body-perturbation-theory method

V. A. Dzuba*
School of Physics, University of New South Wales, Sydney, 2052, Australia

W. R. Johnson
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

(Received 17 October 1997)

A recently developed method of precise atomic calculations [Phys. Rev. A **54**, 3948 (1996)] which combines many-body perturbation theory with the configuration-interaction method is used to calculate the 24 lowest energy levels of Ba. *B*-spline functions in a cavity of a finite radius are used as a unified many-purpose basis set. The calculation reproduces the experimental removal energies for Ba within a fraction of a per cent. Advantages of the new method and *B* splines are discussed. [S1050-2947(98)04604-6]

PACS number(s): 31.15.Ar, 31.15.Md, 31.15.Pf

I. INTRODUCTION

Recent measurements of parity nonconservation (PNC) effects in atoms emphasize the need for high-precision atomic structure calculations in heavy atoms. The latest achievement in this field was the first observation of the nuclear anapole moment [1]. The contributions of the nuclear anapole moment and other spin-dependent weak interactions to PNC in cesium have been extracted by comparing the PNC for different components of the hyperfine multiplet. The accuracy of the measurement of the spin-independent PNC effect was 0.35% in this experiment. Earlier, an accuracy of ~1% in atomic PNC measurements was achieved for Tl [2], Pb [3], and Bi [4]. Interpretation of these experiments is now limited by the uncertainty in the theory. The accuracy of atomic PNC calculations is about 1% for alkali-metal atoms [5–7], while for other atoms it is considerably lower, e.g., for Tl, Pb, and Bi, it ranges from 3% to 10% [8,9]. Further improvement in the theoretical accuracy can probably be achieved for alkali-metal atoms within the framework of existing methods [5–7], whereas for atoms with more than one external electron new ideas are required.

The main source of error in calculations of many-electron atoms is electron correlations. It is well understood now that certain sequences of the correlation diagrams should be included in all orders to obtain accurate results. There are few all-order techniques available at present time. The most popular one is probably a coupled cluster (CC) approach [10], in which correlation terms are grouped by the number of excited particles rather than by the order of the perturbation theory. Most of the existing implementations of the CC approach include pair correlations in all orders, but neglect triple and higher correlations. However, as demonstrated in Ref. [11], even for alkali-metal atoms triple correlations are important if better than 1% accuracy is needed. Owing to computer limitations and other technical difficulties, only selected triple and quadrupole excitations can be included in CC calculations. Although extending the CC approach to include many-particle correlations is one way to improve the accuracy of atomic structure calculations, alternatives should also be considered. An all-order technique, developed in Ref. [12], uses a different approach to group diagrams in infinite series; associating them with different correlation effects in atoms. Three dominating chains of diagrams have been revealed and summed to all orders: (a) screening of the Coulomb interaction, (b) the hole-particle interaction, and (c) iterations of the self-energy operator. This alternative method is not restricted to pair correlations, since the Feynman diagram technique used in Ref. [12] includes all possible time ordering of the loops, therefore, screening diagrams contain any number of excited electrons. This approach gives very good results for alkali-metal atoms [12], where a single external electron is well separated from all other atomic electrons. However, it does not work well for atoms other than alkalis, especially for atoms with more than one valence electron, because the omitted higher-order diagrams become important here [12].

An obvious way to account for the correlations between the valence electrons fully is direct diagonalization of the many-electron Hamiltonian matrix. This is done in the configuration-interaction (CI) method [13]. However, relatively few core excitations can be included into matrix diagonalization owing to a rapid increase of the matrix size. Thus most of the core-valence correlations are not included. A way to incorporate most of the core-valence correlations (e.g., all second-order correlations) into CI calculations was suggested in Ref. [14]. In that work, correlations between the valence and core electrons were calculated by means of a many-body perturbation theory (MBPT). They were then included into the CI matrix in the form of corrections to the matrix elements, while the size of the matrix remained unaffected. The precision obtained in Ref. [14] for the energy levels of Tl was better than 1%. This means that both the core-valence and valence-valence correlations are treated quite accurately by the new method. As found in Ref. [14], the major factor limiting the effectiveness of the method and thus the accuracy of the final results is the choice of the

---

*E-mail: V.Dzuba@unsw.edu.au
http://www.phys.unsw.edu.au/~dzuba/

valence-electron basis set. Hence, we now try to improve the new method along this line.

In the present paper, we show that the method can be made much more effective by introducing a *B*-spline [15] basis set. Intensive use of *B* splines in atomic calculations began about ten years ago [16], and since then their popularity has been growing (see, e.g., Ref. [17]). The reason is that *B* splines have the remarkable property of providing effective completeness with a relatively small number of basis functions. By incorporating them into the combined CI+MBPT method, we can significantly improve its convergence and numerical accuracy. This allows us to calculate a whole series of states of barium with high accuracy.

There are several reasons to choose barium for our calculations. First, the barium atom is a candidate for future measurements of PNC in atoms [18]. Therefore, it is important to assess the theoretical accuracy that can be achieved for this atom. On the other hand, barium is a good object to test the new technique, since it has a relatively simple electronic structure with only two valence electrons. Even so, correlations between the valence electrons and with the core are strong, and must be treated to a high level of accuracy to obtain good results.

II. METHOD

A detailed description of the combined CI+MBPT method was given in Ref. [14]. We briefly repeat it here emphasizing the role of the single-electron basis set.

A. Starting approximation

It is widely accepted that the best starting point for MBPT calculations is the Hartree-Fock approximation. This is because certain classes of the MBPT diagrams cancel each other exactly, simplifying MBPT significantly. Thus first-order terms vanish completely, while the number of second-order diagrams decreases several times. In the case of barium, the MBPT would have its simplest form in the V^{N-2} approximation, in which the self-consistent potential is determined for the Ba^{2+} ion, and the states of the external electrons are calculated in the field of the frozen core. However, in calculations for a neutral atom, starting from a double ion can lead to a slow convergence and an underestimate of the core-valence correlation correction. Therefore, we prefer to work in the V^N approximation. This slightly compromises the simplicity of the MBPT: a new class of ‘‘subtraction’’ diagrams appears [14]. Nevertheless, the MBPT is still relatively simple, and the advantage of having a more realistic starting approximation justifies the compromise. Note also that we use the relativistic Hartree-Fock method or, as it is often called, the Dirac-Hartree-Fock method.

B. Configuration interaction

As mentioned above, full-scale CI calculations are not feasible for atoms such as barium. Therefore, following the standard approach, we fix all states below 6*s* and consider them as a core. No core excitations are allowed at this stage. A many-electron wave vector describing an atomic state with angular momentum J,M may be written

$$\Psi_{JM}=\sum_I c_I\Phi_I, \tag{1}$$

where c_I are expansion coefficients to be determined by the variational principle and the configuration state vectors Φ_I are defined by

$$\Phi_I\equiv\Phi_{ij}=\eta_{ij}\sum_{m_i m_j} C^{JM}_{j_i m_i j_j m_j} a_i^\dagger a_j^\dagger|0\rangle, \quad i\leqslant j; \tag{2}$$

with

$$\eta_{ij}=\begin{cases}1 & \text{if } i\neq j\\ 1/\sqrt{2} & \text{if } i=j.\end{cases} \tag{3}$$

$C^{JM}_{j_i m_i j_j m_j}$ designates a Clebsh-Gordan coefficient, $a_i^\dagger$ is the creation operator for the electron in valence state i, and $|0\rangle$ is the state function for the frozen Hartree-Fock core $(1s,2s,\ldots,5p)$. Variation with respect to c_I leads to a matrix eigenvalue problem (see, e.g., Ref. [14])

$$\sum_I \left(\langle\Phi_I|H^{\mathrm{CI}}|\Phi_J\rangle-E_{\mathrm{val}}\delta_{IJ}\right)c_I=0. \tag{4}$$

Here E_{val} is the energy of the valence electrons, and H^{CI} is the effective CI Hamiltonian acting in the valence space:

$$\begin{aligned} H^{\mathrm{CI}}&=h(r_1)+h(r_2)+\frac{e^2}{r_{12}},\\ h(r)&=c\boldsymbol{\alpha p}+(\beta-1)mc^2-\frac{Ze^2}{r}+\hat{V}_{\mathrm{core}}(r), \end{aligned} \tag{5}$$

where $V_{\mathrm{core}}(r)$ is the Hartree-Fock potential created by the core electrons. Note that the 6*s* state does not contribute to V_{core}.

The eigenvalue problem (4) corresponds to the standard CI method. Prohibiting excitations from the core means that no correlations between the core and valence electrons are included in Eq. (4). One of the possible ways to include correlations with the core is to extend Eq. (1) to allow for selected core excitations. However, this leads to a rapid increase of the matrix size in Eq. (4). On the other hand, as is known from a number of MBPT calculations, the core-valence correlation energy is spread over large number of terms, no term being dominant. Thus only a small fraction of the core-valence correlations can be included in this way. This significantly restricts the accuracy of the CI calculations for many-electron atoms. Another way to include core-valence correlations, suggested in Ref. [14], is to use MBPT instead; this approach is used in the following section.

C. Inclusion of core excitations

Now, following Ref. [14], we extend expansion (1) to allow for excitations from the core

$$\Psi_{JM}=\sum_I c_I\Phi_I+\sum_K c'_K\Phi'_K, \tag{6}$$

with

$$\Phi'_K=\begin{cases} a_i^\dagger a_j^\dagger a_k^\dagger a_n|0\rangle & \text{single excitations} \\ a_i^\dagger a_j^\dagger a_k^\dagger a_l^\dagger a_n a_m|0\rangle & \text{double excitations} \\ \ldots & \text{higher excitations,} \end{cases} \tag{7}$$

where a_n creates a hole in the core state n.

Considering the second term in Eq. (6) as a perturbation, varying c_I, and keeping the perturbation in the lowest nonvanishing order, we obtain the following equations (see Ref. [14] for details):

$$\sum_I \left(\langle \Phi_I | H^{\mathrm{CI}} | \Phi_J \rangle + \sum_K \frac{U_{IK}U_{KJ}}{E_{\mathrm{val}}-E_K} \right) c_I = E_{\mathrm{val}} c_J, \tag{8}$$

where E_K is the energy of the virtual configuration which has single or double excitation from the core: $E_K=\Sigma_{i=\mathrm{particles}}\epsilon_i - \Sigma_{j=\mathrm{holes}}\epsilon_j$, $U_{IK}\equiv\langle\Phi_I|\hat{U}|\Phi'_K\rangle$, and

$$\hat{U}=\sum_{i<j}\frac{e^2}{r_{ij}}-\sum_i V^N(r_i)$$

is the residual Coulomb interaction. Equations (8) are the main equations of the combined CI+MBPT method. They differ from the standard CI equations (4) by the second-order term with respect to residual Coulomb interaction $\hat{U}$. As seen from Eq. (8), application of the lowest-order MBPT is justified when the residual Coulomb interaction is small compared to the excitation energies of the core. In particular, this means that a division of atomic electrons into valence and core electrons should be done so as to maintain a sufficient energy gap between the core and valence states. Note that inclusion of the core-valence correlations by means of MBPT leads to a correction in the effective Hamiltonian,

$$H^{\mathrm{CI}}\rightarrow H^{\mathrm{CI}}+\sum_K \frac{\hat{U}|K\rangle\langle K|\hat{U}}{E_{\mathrm{val}}-E_K}, \tag{9}$$

while the expression for the wave function (1) remains the same as in the standard CI method. It should also be noted that restricting the perturbation expansion to the second order means that only single and double excitations from the core are included in Eq. (7). Thus the maximum total number of electron excitations in Ba is four (in Tl in Ref. [14], the maximum total number of electron excitations was five). In this sense, the present method goes far beyond pair correlations.

To calculate the second-order core-valence correlation term, we use a diagram technique described in detail in Ref. [14]. To calculate the diagrams and evaluate the effective CI matrix, we need a complete basis set of one-electron functions.

D. *B*-spline basis set

There are two points in the method where completeness of the basis set needs to be achieved: (1) Calculation of the second-order MBPT terms in Eq. (8) involves infinite single or double summations over intermediate states. Saturation of these sums corresponds to an effective completeness of the basis used for these states. (2) Decomposition of the two-particle wave function of the valence electrons (1) must also be reasonably complete. It is convenient to use the same basis set for both purposes, although this is not absolutely necessary. Since the core states are fixed, the only conditions imposed on the basis states for valence electrons are the following. They must provide effective completeness and be orthogonal to the core states. In principle, any basis set which satisfies these conditions can be used for the calculations. For example, three different basis sets were used in Ref. [14]:

(1) Single-electron eigenstates of the Hartree-Fock operator in the discrete and continuum spectra. This basis set was used to calculate the MBPT diagrams only. It was not appropriate for the construction of many-electron wave function for the CI calculations, because of slow convergence.

(2) State-dependent basis functions having fixed asymptotic form. These were calculated using the same Hartree-Fock Hamiltonian, but different boundary conditions. That is, their long-range form was chosen to fit the known experimental ionization potential from a particular state. This basis set was not suitable for a calculation of the diagrams due to its lack of completeness for this purpose. However, the convergence for the CI calculations was extremely fast. Actually, the use of this basis set demonstrated that convergence can be very much improved by adjusting the basis to a particular state (or group of states), and thereby reducing the number of terms in the decomposition for the state(s). The use of *B* splines, discussed below, is another way to accomplish this.

(3) A combination of polynomials with eigenstates of the Hartree-Fock Hamiltonian. This basis set has the advantage of being suitable for both the diagram calculation and the construction of the many-electron wave function. However, the convergence was not particularly good.

In the present paper we use a basis set constructed from *B* splines. We follow deBoor [15], and use the software routines described therein. To construct a coordinate grid we consider the atom to be in a cavity of radius R. Atomic wave functions are assumed to be zero for $r\geqslant R$. The interval $[0,R]$ is divided into n segments by the knot sequence t_i. The knot points are distributed on $[0,R]$ on an exponential scale, with smaller intervals at the origin and larger intervals at large distances. *B*-spline basis functions $B_{i,k}$ are piecewise polynomials of degree $k-1$ inside the interval $t_i\leqslant r<t_{i+k}$; they vanish outside this interval. The set of *B* splines of order k on the knot sequence $\{t_i\}$ forms a complete basis for piecewise polynomials of degree $k-1$ on the interval spanned by the knot sequence. It is natural to assume that any smooth function with a limited number of nodes can be approximated to very high precision by piecewise polynomials. This means that the $B_{k,i}$ basis set is complete for these functions too. In our calculations for Ba we use $n=40$, $k=7$, and $R=40a_0$ (a_0 is the Bohr radius).

In principle, the *B*-spline basis set $B_{i,k}$ can be directly used to solve Eqs. (4) or (8). However, it is not convenient to do so because the functions $B_{i,k}(r)$ are not orthogonal to each other and to the core states. Instead, we construct orthonormalized combinations of the *B* splines by diagonalizing the matrix of the Hartree-Fock Hamiltonian

$$\sum_i (\langle B_{i,k}|H^{\mathrm{HF}}|B_{j,k}\rangle - E\delta_{ij})c_i=0, \tag{10}$$

TABLE I. Energies (in a.u.) of the single-particle s states of Ba in a cavity of radius $R=40a_0$.

n	B splines	Accurate numerical solution
1	−1383.8365	−1383.8365
2	−222.5776	−222.5776
3	−48.6516	−48.6516
4	−10.2573	−10.2573
5	−1.6035	−1.6035
6	−0.1631	−0.1631
7	0.0044	0.0043
8	0.0176	0.0174
9	0.0391	0.0388
10	0.0685	0.0681
11	0.1059	0.1054
12	0.1493	0.1487
13	0.2778	0.1992
14	0.3383	0.2565
15	0.6548	0.3205
16	1.6740	0.3912
17	4.6333	0.4684
18	13.6900	0.5523
19	42.4656	0.6428
20	131.7190	0.7398
21	165.9604	0.8433
22	381.4315	0.9534
23	1003.1873	1.0700
24	2382.6952	1.1930
25	5122.8775	1.3226
26	10 048.0796	1.4596
27	18 197.4531	1.6010
28	30 907.3301	1.7499
29	50 016.4662	1.9052
30	78 228.4827	2.0669
31	119 575.1598	2.2350
32	180 321.4070	2.4095
33	270 192.1563	2.5904
34	405 671.8233	2.7777
35	614 983.5032	2.9713
36	957 203.1898	3.1713
37	1 563 072.3099	3.3776
38	2 892 240.5288	3.5903
39	7 107 212.9123	3.8093
40	48 924 980.8393	4.0346

$$H^{\mathrm{HF}}(r)=c\boldsymbol{\alpha}\boldsymbol{p}+(\beta-1)mc^2-\frac{Ze^2}{r}+V^N(r). \tag{11}$$

Note that unlike for V_{core} in Eq. (5), $6s$ electrons also contribute to the V^N. Eigenstates of Eq. (10) are variational finite-basis solutions of the atomic Hartree-Fock problem in the cavity of radius R. In Table I we compare the energy spectrum of Eq. (10) for the s states with the actual spectrum of the problem which was obtained by accurate numerical solution of the Hartree-Fock equation $H^{\mathrm{HF}}(r)\psi(r)=E\psi(r)$ with the boundary condition $\psi(R)=0$. The energies must be the same if the B-spline basis set is complete. As seen from the table, for $n\leqslant 6$ the energies coincide precisely. For $n\geqslant 7$ the energies of B-spline states start to deviate from the accurate values, and for $n>13$ they differ significantly. This means that a set of 40 splines is incomplete for the highly excited rapidly oscillating states. However, it is complete with very high precision for the lowest states.

TABLE II. Two-electron energies E_{val} of the Ba ground state in different approximations (a.u.)

RHF[a]	MBPT[b]	CI[c]	CI+MBPT[d]	Experiment[e]
−0.504 02	−0.540 53	−0.527 90	−0.560 65	−0.559 15

[a] Single-configuration approximation. No correlations are included.

[b] Single-configuration approximation. Core-valence correlations are included.

[c] Standard CI method (4). Only valence-valence correlations are included.

[d] CI+MBPT method (8). Core-valence and valence-valence correlations are included.

[e] This is the sum of the ionization potentials of Ba and Ba$^+$; Ref. [19].

It is interesting to note that if the eigenstates of Eq. (10) are used in the CI calculations [Eqs. (4) or (8)], then the number of basis states which contribute significantly to the many-electron wave function (1) is considerably smaller than the number of splines n. Indeed, if configuration mixing is treated perturbatively, then the mixing of two basis states would be inversely proportional to the energy interval between them. But, as can be seen from Table I, the higher B-spline eigenstates have very large energies, which means that their admixture to the lower states is negligible. Note that if accurate numerical solutions of the Hartree-Fock problem in a cavity (next column of Table I) are used instead as basis functions for the CI calculations, then the number of the mixed components would be considerably larger. This means that the convergence improves significantly if B splines are used. This improvement is achieved by sacrificing the completeness of the basis for higher states. Since lower states are always of most interest, one can say that B splines provide a very effective and natural way to adopt the basis to the problem of interest. Moreover, it is still possible to consider the higher states if appropriate adjustments of the B-spline parameters n, k, and R are made.

III. RESULTS

Using the technique described above, we have calculated the energies of the 24 lowest states of Ba. To illustrate the role of different terms in Eq. (8), in Table II we present the two-electron energies E_{val} of the barium ground state obtained in different approximations and compare them with the experiment. The relativistic Hartree-Fock (RHF) value in the first column is just the matrix element

$$\langle 6s^2J=0,M=0|H^{\mathrm{CI}}|6s^2J=0,M=0\rangle\equiv 2\epsilon_{6s}-F_0(6s,6s). \tag{12}$$

$\epsilon_{6s}=-0.16318$ a.u. is the Hartree-Fock energy of the 6s state, and $F_0(6s,6s)=0.17766$ a.u. is the direct Coulomb integral of zero multipolarity. Neither the core-valence nor the

TABLE III. Excitation energies of Ba (cm^{-1}).

State		Experiment [19,20]	Present work *A*[a]	Present work *B*[b]	Other calculations
			Even states		
$6s5d$	$^3D_1$	9034	9366	9061	9241[c], 9423[d], 11 164[e]
	$^3D_2$	9216	9552	9246	9429[c], 9631[d],11 280[e],12 126[f]
	$^3D_3$	9597	9946	9643	9818[c],10 065[d], 11 492[e]
$6s5d$	$^1D_2$	11 395	11 871	11 527	11 841[c],13 164[e], 13 677[f]
$5d^2$	$^3F_2$	20 934	22 021	21 474	21 334[c], 23 570[e]
	$^3F_3$	21 250	22 348	21 800	21 663[c], 23 710[e]
	$^3F_4$	21 624	22 742	22 194	22 060[c], 23 894[e]
$5d^2$	$^1D_2$	23 062	24 151	23 608	24 256[c], 25 427[e]
$5d^2$	$^3P_0$	23 209	24 311	23 765	24 218[c], 24 435[e]
	$^3P_1$	23 480	24 637	24 090	24 427[c], 24 703[e]
	$^3P_2$	23 919	25 072	24 526	24 943[c], 24 867[e]
$5d^2$	$^1G_4$	24 300(300)	26 145	25 597	25 585[c], 29 435[e]
$5d^2$	$^1S_0$		26 444	26 034	29 167[e]
$6s7s$	$^3S_1$	26 160	26 277	26 104	
	$^3S_0$	28 230	28 634	28 327	
			Odd states		
$6s6p$	$^3P_0$	12 266	12 573	12 300	12 503[c], 12 221[d]
	$^3P_1$	12 637	12 936	12 661	12 882[c],12 583[d], 11 902[f]
	$^3P_2$	13 515	13 821	13 548	13 792[c], 13 448[d]
$6s6p$	$^1P_1$	18 060	18 347	18 031	18 455[c],17 740[d], 17 393[f]
$5d6p$	$^3F_2$	22 065	22 662	22 117	22 705[c]
	$^3F_3$	22 947	23 513	22 968	23 632[c]
	$^3F_4$	23 757	24 336	23 791	24 491[c]
$5d6p$	$^1D_2$	23 074	23 730	23 183	23 823[c]

[a] Pure *ab initio* results.

[b] Higher-order core-valence correlations are included semiempirically by decreasing a second-order term in the s channel by 7.6%.

[c] Relativistic coupled-cluster method [21].

[d] CI+MBPT (relativistic) [22].

[e] Multiconfiguration Dirac-Fock method [23].

[f] Multiconfiguration Dirac-Fock method [24].

valence-valence correlations are included in Eq. (12). The value in the second column is the matrix element

$$\left\langle 6s^2 J=0,M=0 \left| H^{\mathrm{CI}}+\sum_K \frac{\hat{U}|K\rangle\langle K|\hat{U}}{E_{\mathrm{val}}-E_K} \right| 6s^2 J=0,M=0 \right\rangle, \tag{13}$$

where $|K\rangle$ represents all possible configurations corresponding to single and double core-valence excitations [see Eq. (4)]. This value includes core-valence correlations in a single-configuration approximation. The values in columns 3 and 4 are the lowest solutions of the matrix eigenvalue problems (4) and (8), respectively. Both values include correlations between valence electrons, but the latter value also includes correlations between the valence and core electrons.

From the values presented in this table, one can see that the correlation correction constitutes about 10% of the total two-electron energy of the barium ground state. About 60% of this correlation energy can be attributed to the core-valence correlations, while the remaining 40% arises from correlations between the valence electrons. Thus, as in the case of Tl [14], the core-valence correlations dominate over the valence-valence ones. However, both types of correlations are very important, and must be included in accurate calculations. The accuracy of the final result $E_{\mathrm{val}}=-0.56065$ a.u. is 0.3%, compared with the experimental value of -0.55915 a.u.

The argument used above to determine the role of the correlations for the ground state of barium is not applicable to the excited states, at least as far as valence-valence correlations are concerned. Indeed, the correlation energy is defined as the difference between the actual energy of the atomic state and its value in the Hartree-Fock approximation. However, the latter is not well defined for an open-shell system. Moreover, the application of MBPT dictates the use of the same potential for all basis states. Since we use the V^N potential, we have no bound valence states above $6s$. Although the continuous spectrum is discretized by putting the atom into a box of finite size, the $7s$, $6p$, $5d$, etc. functions obtained in this way are very different from what they are supposed to be in the $6s7s$, $6s5d$, $6s6p$, etc. excited states of Ba. This leads to a strong configuration mixing for excited states. In principle, this mixing can be reduced significantly by an appropriate choice of one-electron basis states. This is usually done when the primary aim of the calculations is to assign a specific configuration to a particular atomic state. Our aim is different—to approximate an atomic wave function to a very high level of precision. This is achieved through the effective completeness of the basis, even though no particular configuration dominates in the resulting many-electron wave function.

As for the role of the core-valence correlations for the excited states, it can be easily investigated by comparing the calculations with and without the second-order correlation term in the expression for the effective CI Hamiltonian (9). These correlations lower the energies of the barium states by 4000–9000 cm^{-1}. This constitutes about 10% of the total two-electron energy, similar to what we find for the ground state.

In Table III, we present the calculated energies of the 24 lowest states of Ba in the format similar to that used by Moore [19], i.e., we show energies with respect to the Ba $6s^2$ ground state. The experimental values and results from other calculations are also included. As can be seen from the numbers in column A of the table, all theoretical intervals are slightly overestimated. This is because the correlation interaction between valence electrons and core is always overestimated by second-order MBPT. The actual correlation correction is usually about 10% smaller; the decrease being caused by the higher-order correlations [12,16,11]. These higher-order correlations can be included semiempirically by introducing a factor $f<1$ into the correlation correction [the second term in Eq. (9)]. Fitting the energy of the Ba ground state with a single factor f_s, which affects only the correlation interaction of the s electrons with the core, gives $f_s=0.924$, in a reasonable agreement with the accurate calculation of the higher-order correlations for other many-electron atoms [12,7,11]. New energy intervals found with the use of f_s are presented in column B of Table III. With only one fitting parameter, all energy intervals are improved significantly. This is because the fitting mostly affects the energy of the ground state. The excited states are less affected; correlation correction is smaller for them due to the remoteness of the excited electrons from the core. The resulting absolute discrepancy with the experimental data is $\leqslant 100\ \mathrm{cm}^{-1}$ for all the configurations except $5d^2$. For the $5d^2$ configuration the discrepancy ranges between 500 and 600 cm^{-1}. We do not see any significant decrease in accuracy for the excited states in spite of the fact that the finite cavity radius ($R=40a_0$), and the limited number of splines $n=40$ should put certain limitations on the accuracy of such states.

There are many other calculations of the energy levels of Ba, as can be seen from Table III. We would like to mention particularly the calculations by Eliav, Kaldor, and Ishikawa [21] and by Kozlov and Porsev [22]. The calculations in Ref. [22] were done using the method of the present paper, but with a different basis set. This probably led to a slower convergence, especially for the excited states. No attempt to include higher-order correlations was made in that work. We note, however, that the results of Ref. [22] are very close to our second-order results (see column A of Table III). The calculations in Ref. [21] were done using a CC approach with pair correlations included in all orders, while triple and higher excitations were neglected. The accuracy of these results are similar to those in the present work, probably because the triple correlations are suppressed for Ba; it has only two valence electrons and triple correlations can appear only in the core-valence interaction.

In conclusion, we would like to summarize the benefits given by the use of B splines in the CI+MBPT method: (1) The same uniform, state-independent, basis set is used for calculations of the core-valence correlation interaction, and for the construction of the two-electron wave functions for the ground and excited states. (2) Fast convergence is achieved in both of these cases. (3) Good accuracy of the Ba energy levels was obtained, not only for the lowest states but for many excited states as well.

ACKNOWLEDGMENTS

One of the authors (V.D.) is grateful to the Physics Department of the University of Notre Dame for the warm reception and hospitality during his visit. We would like to thank G. Gribakin for reading the manuscript and making useful comments. The work of W.R.J was supported in part by Grant No. PHY-95-13179 from the National Sceince Foundation.

---

[1] C. S. Wood, C. S. Bennett, D. Cho, B. P. Masterson, J. L. Roberts, C. E. Tanner, and C. E. Wieman, Science **275**, 1759 (1997).

[2] N. H. Edwards, S. J. Phipp, P. E. G. Baird, and S. Nakayama, Phys. Rev. Lett. **74**, 2654 (1995); P. A. Vetter, D. M. Meekhof, P. K. Majumder, S. K. Lamoreaux, and E. N. Fortson, *ibid.* **74**, 2658 (1995).

[3] D. M. Meekhof, P. A. Vetter, P. K. Majumder, S. K. Lamoreaux, and E. N. Fortson, Phys. Rev. A **52**, 1895 (1995); S. J. Phipp, N. H. Edwards, P. E. G. Baird, and S. Nakayama, J. Phys. B **29**, 1861 (1996).

[4] M. J. D. Macpherson, K. P. Zetie, R. B. Warrington, D. N. Stacey, and J. P. Hoare, Phys. Rev. Lett. **67**, 2784 (1991).

[5] V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, Phys. Lett. A **141**, 147 (1989).

[6] S. A. Blundell, W. R. Johnson, and J. Sapirstein, Phys. Rev. Lett. **65**, 1411 (1990).

[7] V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, Phys. Rev. A **51**, 3454 (1995).

[8] V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, J. Phys. B **20**, 3297 (1987).

[9] V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, Europhys. Lett. **7**, 413 (1988).

[10] I. Lindgren and J. Morrison, *Atomic Many-Body Theory*, 2nd ed. (Springer-Verlag, Berlin, 1985).

[11] S. A. Blundell, W. R. Johnson, and J. Sapirstein, Phys. Rev. A **43**, 3407 (1991).

[12] V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, J. Phys. B **20**, 1399 (1987); Phys. Lett. A **131**, 461 (1988); V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, *ibid.* **140**, 493 (1989); V. A. Dzuba, V. V. Flambaum, A. Ya. Kraftmakher, and O. P. Sushkov, *ibid.* **142**, 373 (1989).

[13] I. P. Grant and H. M. Quiney, Adv. At. Mol. Phys. **23**, 37 (1988).

[14] V. A. Dzuba, V. V. Flambaum, and M. G. Kozlov, Phys. Rev. A **54**, 3948 (1996).

[15] C. deBoor, *A Practical Guide to Splines* (Springer, New York, 1978).

[16] W. R. Johnson and J. Sapirstein, Phys. Rev. Lett. **57**, 1126 (1986); W. R. Johnson, M. Idrees, and J. Sapirstein, Phys. Rev. A **35**, 3218 (1987); W. R. Johnson, S. A. Blundell, and J. Sapirstein, *ibid.* **37**, 307 (1988).

[17] J. E. Hansen, M. Bentley, H. W. van der Hart, M. Landtman, G. M. S. Lister, Y.-T. Shen, and N. Vaeck, Phys. Scr. **T47**, 7 (1993); J. Sapirstein and W. R. Johnson, J. Phys. B **29**, 5213 (1996).

[18] X. Xiaxing, H. Mouqi, Z. Youyuan, and Z. Zhiming, J. Phys. B **23**, 4239 (1990); P. K. Majumder and E. N. Fortson (private communication).

[19] C. E. Moore, *Atomic Energy Levels,* Natl. Bur. Stand. Circ. No. 467 (U.S. GPO, Washington, DC, 1958), Vol. III.

[20] S. G. Schmelling and G. O. Brink, Phys. Rev. A **12**, 2498 (1975); H. P. Palenius, Phys. Lett. A **56**, 451 (1976); J. R. Rubbmark, S. A. Borgstrom, and K. Bockasten, J. Phys. B **10**, 1803 (1977).

[21] E. Eliav, U. Kaldor, and Y. Ishikawa, Phys. Rev. A **53**, 3050 (1996).

[22] M. G. Kozlov and S. G. Porsev, Zh. Éksp. Teor. Fiz. **111**, 838 (1997) [Sov. Phys. JETP **84**, 461 (1997)].

[23] S. G. Rose, N. C. Pyper, and I. P. Grant, J. Phys. B **11**, 755 (1978).

[24] J. Migdalek and W. E. Baylis, Phys. Rev. A **35**, 3227 (1987); **42**, 6897 (1990).