

Excitation energies and oscillator strengths of Ca I using multireference many-body perturbation theory

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Excitation energies and oscillator strengths of neutral calcium (Ca I) are calculated through third order using a variant of the multireference many-body perturbation theory, known as the effective valence-shell Hamiltonian (H^v) method. Transition energies, oscillator strengths, and binding energies of various states are computed and compared with experimental and other theoretical data. These quantities are in favorable agreement with the experiment and other correlated calculations. The basis and valence space dependence of the H^v scheme are addressed with some illustrative examples. [S1050-2947(99)06905-X]

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I. INTRODUCTION

Atomic transition lines of neutral calcium were first found in solar spectrum as early as the middle of the 19th century, when the 4227-Å line was identified along with the famous singly ionized H and K lines [1]. Neutral calcium lines have also been observed in all types of stellar and interstellar spectra, such as late-type dwarf stars. The crude abundance of Ca I ($\lambda = 6717.7$ Å) has been observed in Am binaries [2]. To confirm those identifications and to find new lines, one has to depend on atomic experimental data or computational data based on theoretical models of the calcium atom. The abundances of neutral calcium in these astronomical bodies depend on the oscillator strengths of those lines, which come from the excitation energies of various levels and transition moments among those levels.

The difficulty in accurately estimating transition energies and oscillator strengths of neutral calcium atom arises mainly due to the following reasons: (a) The precise computation of transition energies and oscillator strengths requires a balanced description of the ground and excited states. (b) The use of an inadequate basis leads to difficulties in describing the excited states and an unbalanced treatment of dynamical correlation and polarization effects. The problems due to basis set inadequacy can be removed partially by enlarging the basis for small and moderate-sized atomic and molecular systems. Here, the size extensivity [3] of the theory plays an important role in handling the proper treatment of electron correlation, and in that way it properly treats the differential correlation energies of the interacting (initial and final states) zeroth-order states. It ensures that the state energies scale linearly with the number of electrons in a rigorous way.

The accuracy of the computed excitation energy depends mostly upon the quality of the unoccupied valence orbitals in which excitation occurs. The traditional choice of some unoccupied valence orbitals from a ground-state self-consistent-field (SCF) computation introduces V^N orbitals that are best suited for describing negative ions, and not low-lying excited states. Thus the valence orbitals, those that are not occupied in the ground-state SCF, should be taken as more representative orbitals suitable for excited states. One

possible choice emerges from the restricted single excitation configuration interaction procedure [4], where excitations are only permitted from the highest occupied orbitals. A simpler and often equivalent approaches involves using improved virtual orbitals (IVO's) [5] in the H^v valence space or reference space. Here the IVO's are generated by single orbital SCF optimization in which the Fock operator is defined by promoting an electron from the highest occupied orbital to the orbital being optimized, while all the previously determined orbitals are kept frozen. Alternatively this can be accomplished by a unitary transformation [6]. The IVO orbital energies obtained in this way are lower than those evaluated from the traditional SCF procedure due to the absence of an extra Coulomb operator in the former procedure. For example, in a neutral calcium atom H^v calculation, the two-orbital ($4s, 4p$) minimal reference space is produced by the sequence

- (1) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 \quad 1^1S_0$
- (2) $[1s^2 2s^2 2p^6 3s^2 3p^6 4s^1] 4p^1 \quad 1^3P_1$.

The first step is a SCF calculation for the ground state and step (2) requires only a single orbital optimization in which the orbitals shown in square brackets are frozen like those determined in the previous steps, i.e., step (1). The excited orbitals are then obtained by diagonalizing the 1^1S_0 state Fock operator in the orbital space complementary to the union of the core and reference spaces.

Successful H^v computations for Mg-like ions [7] have stimulated us to try this scheme for a neutral calcium atom (Ca I) and, in this paper, we present the theoretically computed excitation energies, binding energies (energy relative to first ionization threshold), and oscillator strengths and transition probabilities of Ca I for a wide range of configurations (nonrelativistically allowed transitions). As mentioned above, these computations are based on the effective valence-shell Hamiltonian (H^v) method proposed by Freed [5]. The H^v method has been found to be quite successful in accurately assigning the electronic spectrum of atomic and complex molecular systems, such as open-shell atoms like neutral carbon [8] and closed-shell atoms (where strongly interacting correlations are present) like conjugated polyenes and inorganic molecules [7,9–11]. By virtue of being a multireference approach, the H^v method incorporates the nondy-

namical correlation necessary to describe open shells and, hence, possesses distinct advantages over the traditional single-reference many-body perturbation theory.

Section II briefly reviews the background theory, while Sec. III describes the computational details. The computed results and discussions are presented in Secs. IV and V, respectively.

II. THEORY

Perturbative methods proceed by first partitioning the exact Hamiltonian H into a zeroth-order part H_0 and a perturbation V ,

$$H = H_0 + V, \quad (2.1)$$

where H_0 contains all one-electron Fock operators. (The decomposition of H , *in principle*, is arbitrary, but *in practice*, proper care must be exercised to avoid introducing numerical instabilities into the perturbative expansions.) The full many-electron Hilbert space is decomposed into a model space (P space) with a projector P and its orthogonal complement space (Q space) with a complement projector $Q = 1 - P$. The P space spans the model space (also called reference or valence space) of all distinct configuration state functions which have all core orbitals doubly occupied, and the remaining electrons are distributed in the valence orbitals in all possible ways, thereby ensuring the ‘‘completeness’’ of the P space. The Q space contains all basis functions with at least one core hole and/or one occupied excited orbital. The H^v method proceeds by transforming the full Schrödinger equation

$$H\Psi_i = E\Psi_i \quad (2.2)$$

into the P -space effective valence-shell Schrödinger equation

$$H^v\Psi_i^v = E\Psi_i^v, \quad (2.3)$$

where the projected wave function is $\Psi_i^v = P\Psi_i$, and E is the exact eigenvalue of the full Hamiltonian. The H^v method gives the unique lowest-order approximation,

$$H^v = PHP + \frac{1}{2} \sum_{\phi, \phi'} \times [P(\phi)VQ(E_\phi - H_0)^{-1}QVP(\phi') + \text{H.c.}], \quad (2.4)$$

where $P(\phi)$ is the projector onto the valence space basis function ϕ , and H.c. denotes the Hermitian conjugate of the preceding term. The computations of excitation energies proceed to the next order (third) in V .

The matrix elements of an operator D are transformed by the H^v theory into

$$\langle \Psi_i | D | \Psi_j \rangle \rightarrow \langle \Psi_i^v | D^v | \Psi_j^v \rangle, \quad (2.5)$$

where D^v is effective valence-shell operator which is computed from D by

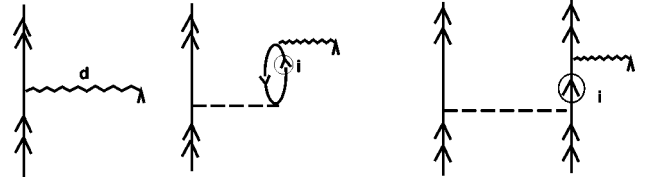


FIG. 1. Typical one- and two-body H^v dipole diagrams. Here the line going up (down) refers to the virtual (core) orbital. The valence orbitals are represented by a line with a double arrow, and a line with an arrow inside a circle can be a valence or virtual orbital.

$$D^v = PDP + \frac{1}{2} \sum_{\phi, \phi'} \times [P(\phi)VQ(E_\phi - H_0)^{-1}QDP(\phi') + \text{H.c.}], \quad (2.6)$$

Many-body theory techniques can be applied to reduce expressions (2.5) and (2.6) to represent the matrix elements of D^v in the valence orbital basis. The resulting equations may be written alternatively in terms of core-, one-, two-, ... electron valence-shell operators D_c^v , D_i^v , D_{ij}^v , ..., respectively, in the operator representation

$$D^v = D_c^v + \sum_i D_i^v + \frac{1}{2} \sum_{i,j} D_{ij}^v + \dots, \quad (2.7)$$

where D is a dipole operator, and D^v is an effective dipole operator that acts only on the P space. It should be noted that although the dipole operator is a one-electron operator, two-electron effective terms D_{ij}^v appear in the nontrivial lowest-order perturbation expansion of Eq. (2.6). This nonclassical two electron term is necessary to obtain accurate dipole transition moments. Figure 1 shows typical one- and two-body diagrams that are zero- and first-order V .

In the actual computation, the effective Hamiltonian H^v is first diagonalized to obtain the desired eigenvalues and eigenfunctions. The latter are then used to compute expectation values and transition moments of some operator D . In the length gauge, the absorption oscillator strength (f) is defined as

$$f_{i \rightarrow f} = \frac{2\Delta E}{3} \left| \left\langle \Psi_f \left| \sum_k \mathbf{r}_k \right| \Psi_i \right\rangle \right|^2 \quad (2.8)$$

where $\Delta E = E_f - E_i$ is the transition energy, and $\langle \Psi_f | r | \Psi_i \rangle$ is the transition moment.

III. COMPUTATIONAL DETAILS

Appropriate selections of the basis set, orbitals, and valence space are difficult, but comprise the most essential task in all *ab initio* many-body methods, because the perturbative convergence of a finite-order calculation strongly depends upon these factors. A prior knowledge of the system of interest may reduce the computational effort to find an optimal basis set and reference space; otherwise some trial and error are required to achieve this goal. We employ a variety of basis sets and reference spaces to study their effect on the

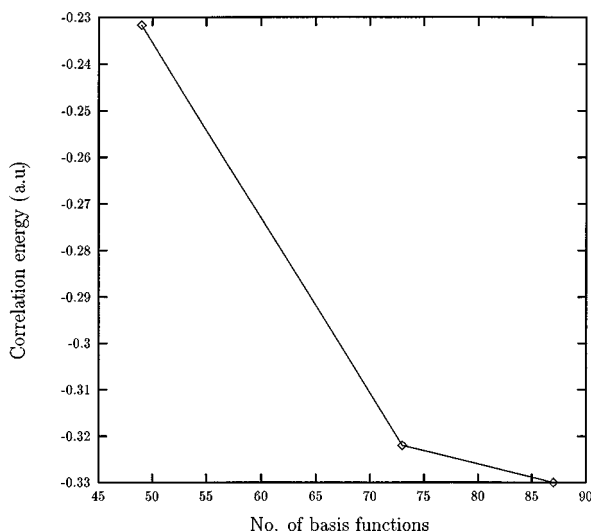


FIG. 2. Variation of the third-order H^v (with 14V reference space) correlation energy as a function of basis set.

computed excitation energies through the third-order H^v method.

We emphasize that there exists a significant difference in the choice of both orbitals and orbital energies between the H^v method and the traditional multireference many-body perturbation theory (MR-MBPT) scheme [5,12–18]. In the MR-MBPT method all orbitals and orbital energies are obtained from a single V^N Fock operator (the ground-state Fock operator), and, therefore, all orbitals (core, valence, and excited) and their energies are evaluated from a V^N potential. The unoccupied reference orbitals are, therefore, more appropriate for describing negative-ion states than for low-lying excited states of interest. On the other hand, the H^v method determines the unoccupied reference space orbitals and their energies as IVO's from a V^{N-1} potential. The unoccupied reference space orbital energies are much lower than those evaluated from V^N potential due to the absence of an extra Coulomb operator in the former. After the H^v valence orbital energies are computed in this above-mentioned fashion, the reference space orbitals are replaced by their democratic average to eliminate (or reduce) the convergence difficulties. The valence orbital energy averaging process introduces an additional diagonal perturbation [5] which appears in the perturbation expansion from third order onwards.

Figure 2 plots the variation of the correlation energy ($E^{\text{third}} - E_{\text{HF}}$) as a function of basis set obtained from 14 V reference space computation (described below), where we find that the correlation energy decreases substantially as the number of basis function increases from 49 to 73. The variation in correlation energy then slows down with further increase in the basis set. Here we employ a moderate size calcium basis (to reduce the computational effort without sacrificing the accuracy) which is constructed from the (12s9p5d/5s4p1d) contracted Gaussian basis of Dobbs and Hehre [19], augmented by one polarized d function ($\zeta_d = 0.100$) and two s ($\zeta_s = 0.011, 0.0056$), one d ($\zeta_d = 0.0416$), and three f ($\zeta_f = 3.0, 1.5, \text{ and } 0.75$) diffused functions and this yields 73 contracted Gaussian-type orbitals (CGTO's). [Some third-order H^v calculations have also

been performed with 87 CGTO's (generated by adding few s , p , and d functions to 73 basis sets). Here we have used D_{2h} symmetry. Since the perturbative convergence of the computed excitation energies and oscillator strengths for this set are close to the smaller one (73 CGTO's), we only report the smaller basis set (73 CGTO's) H^v results.]

The valence orbitals are selected on the basis of their orbital energies (to avoid the near degeneracies among the reference and virtual space states) and their relative importance in properly describing the excited states of interest, i.e., in providing an accurate first-order description to minimize the perturbative corrections. This selection is almost mandatory in all MR-MBPT method to mitigate the so-called *intruder-state* problem [20] that arises due to the near degeneracy of the reference and virtual space states and their relative ordering [21]. The reference space must include the 4s (the outermost occupied) orbital and 4p (lowest-lying unoccupied) orbital for describing the lowest-lying states of S and P multiplets which arises from $4s \rightarrow 4p$ transition. [Note that the ground state (1S_0) of the neutral calcium atom is mostly dominated by [Ar]4s² (91%) and [Ar]4p² configuration state functions (CSF's) [22].] Therefore, the minimal reference space contains only the 4s and 4p orbitals with two active electrons in the active space. Since a minimal reference space {4s,4p} provides an inadequate description of excited states (CSF's [Ar]4s4p (80%) and [Ar]4p3d (16%) contribute 96% to the first excited singlet state of P symmetry [22]) and, moreover, since we are interested in both the lowest-lying and higher-lying states, we extend the valence space carefully to avoid the near-degeneracy of the reference and virtual space states as much as possible in order to reduce the perturbative convergence problem. Thus, our first extended valence space is made of 4s, 4p, 5s, and 5p orbitals (called 8V; according to D_{2h} symmetry p orbitals has symmetry with respect to three axes, i.e., p_x , p_y , and p_z). Although the computed transition energies obtained from the 8V reference space matches favorably well with the experiment and other correlated calculations for the low-lying excited states of S and P multiplets, it fails to provide an acceptable transition energies for D multiplets as well as the high-lying excited states of S and P multiplets, e.g., 3^1S_0 , 4^1S_0 , 2^1P , etc. The origin of this discrepancy can be traced back from the earlier work of Ref. [22], where it was shown that the 3^1S_0 excited states of neutral calcium is mainly described by the CSF [Ar]4s6s (94%) whereas for the 4^1S_0 excited state the major contribution comes from the CSF's [Ar]4s7s (10%), [Ar]4p² (45%), and [Ar]3d² (38%), respectively. Since, the orbitals 3d, 6s, and 7s are not included in 8V H^v reference space, it is expected that these excited states will be poorly described by the H^v method, and so will their transition energies. Similar arguments also apply to the transition energies of D and F multiplets. Therefore, in order to improve the accuracy of the above-mentioned problematic excited states it is necessary to include the 3d, 6s, and 7s orbitals. Unfortunately, little leeway exists in extending the valence space by including the 7s orbital alone, because these orbitals are near degenerate compared to 4d, 4f, 6p, and 7p orbitals, respectively. Inclusion of 4d, 4f, 6s, 6p, 7s, and 7p orbitals into the reference space will, of course, improve the first-order description of the excited states, but it will severely affect the

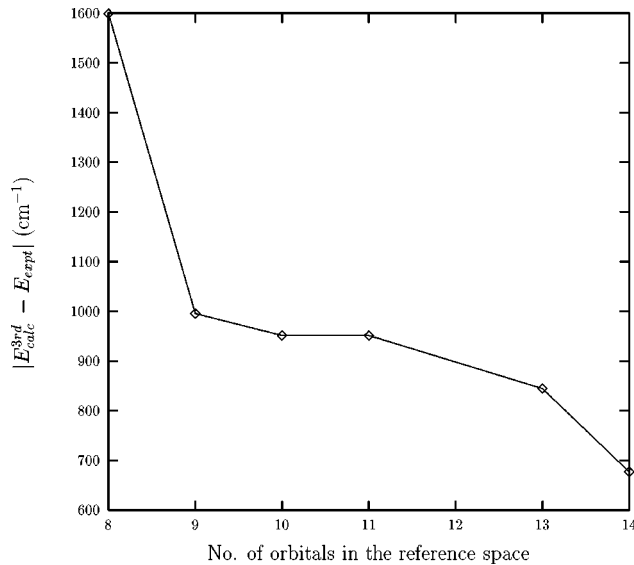


FIG. 3. Variation of the third-order H^v $4s^2 \rightarrow 4s5s(^1S)$ transition energy as a function of number of valence orbitals in the reference space.

perturbative convergence due to the presence of *intruder states* and large diagonal perturbation that appears from the third order onwards due to the valence orbital degeneracy condition. (Note that, as the number of valence space orbitals increases, the quasidegeneracy among the valence orbitals decreases sharply, with a consequent increase in the diagonal

perturbation.) Moreover, the presence of a large number of valence orbitals in the reference space will reduce the computational efficiency of the post Hartree-Fock calculation. Therefore, an optimal set of valence orbital spaces is required which will neither reduce the computational efficiency of the post-Hartree-Fock calculation nor introduce a serious convergence problem *at least* at low order. Based on the earlier work of Ref. [22] on a neutral calcium atom, we construct a complete active H^v reference space (to ensure the size extensivity) by allocating the two active electrons of $4s$ orbitals among $4s$, $4p$, $3d$, $5s$, $5p$, and $6s$ ($14V$) in all possible way. Some typical results obtained from a series of third-order H^v calculations with varying reference are depicted in Fig. 3, which displays the variation of third-order H^v excitation energies as a function of the valence space, respectively. Figure 3 indicates that the accuracy of the computed transition energies sharply increases with the increasing size of the reference space.

IV. RESULTS AND DISCUSSION

The third-order H^v binding energies (energy relative to the first ionization potential) are compared with the experimental data and with other theoretical values which were obtained by using multiconfiguration Hartree-Fock (MCHF) [22], configuration interaction (CI) [23], Spline-Galerkin (SG) [24], and model-potential (MP) methods [25] in Table I. This table clearly demonstrates that the accuracies of our

TABLE I. Low-lying binding energies (in cm⁻¹) of Ca I.

Terms	States	Expt. ^a	MCHF ^b	CI ^c	SG ^d	MP ^e	H^v
Singlet states							
$4s^2$	1S	49 306.0	47 649.0	47 600.5	48 930.31	49 278.3	48 420.28
$4s5s$	1S	15 988.7	15 729.3	15 720.5	15 935.28	15 966.5	15 989.32
$4s6s$	1S	8615.5	8277.6	8270.5	8599.40	8536.0	7625.89
$4p^2$	1S	7519.7	6709.7	6585.1	7887.13	7606.2	10 231.19
$4s4p$	1P	25 653.7	24 689.2	24 667.6	25 472.25		257 20.66
$4s5p$	1P	12 574.3	12 160.1	12 143.3	12 683.80		12 127.36
$4s3d$	1D	27 456.3	24 869.2	24 404.7	27 478.99	27 365.8	26 123.48
$4p^2$	1D	8586.1	7402.9		8802.75		8992.11
Triplet states							
$4s5s$	3S	17 766.0		17 461.4		17 765.7	17 590.5
$4s6s$	3S	8831.2		8714.0		8831.1	8355.2
$4s4p$	3P	34 042.5		34 076.7	34 851.67		33 986.6
$4s5p$	3P	12 740.3		12 570.2	12 899.61		12 334.3
$4p^2$	3P	10 797.7		11 120.1			11 675.8
$3d^2$	3F	5811.7		835.7		5811.6	5381.1
$3d4p$	3F	13 474.2		10 797.9	14 032.06		12 244.7
$4s3d$	3D	28 948.9		24 293.0	28 096.19		27 413.2
$3d4p$	3P	9967.6		7148.3	9866.51		7392.3
$3d4p$	3D	11 073.1		6881.8			8218.1

^aReference [29].

^bReference [22].

^cReference [23].

^dReference [24].

^eReference [25].

calculations of the third-order H^v binding energies for singlets (average deviation $\approx 855 \text{ cm}^{-1}$) are better than those of the MCHF (average deviation $\approx 1027 \text{ cm}^{-1}$) and CI calculations (average deviation $\approx 1103 \text{ cm}^{-1}$), though the number of configurations used in the latter calculations are much larger than ours. This demonstrates the power of the MR-MBPT approach in general and the H^v method in particular. This approach is computationally more efficient than the MCHF and CI methods, since it includes strongly interacting configurations in the model space and relating weakly interacting configurations which lie in the complementary space are treated perturbatively. The SG and MP calculations for the binding energies are in general in better agreement with experimental than ours. Table I clearly indicates that our results are consistently better than those obtained by the CI method. For example, for the triplet states the average deviation for our calculations is 1061 cm^{-1} , while for the CI calculations it is 2026 cm^{-1} . This suggests that the H^v method treats the differential correlation more accurately than the MCHF and CI methods. Despite the fact that the H^v method provides accurate estimate of the binding energies for most of the excited states, it fails to produce an accurate binding energy for the 4^1S excited states (it deviates by 2711.5 cm^{-1} from experiment). The underlying reason for this large deviation in the estimated binding energy of the 4^1S excited state becomes transparent when we analyze the composition of the 4^1S excited state in terms of CSF's. The MCHF calculation of Ref. [22] and other calculations show that this particular singlet excited state is multiconfiguration in nature, where the major contribution comes from the CSF's $[\text{Ar}]4p^2$ (46%), $[\text{Ar}]3d^2$ (39%), $[\text{Ar}]4s7s$ (10%), $[\text{Ar}]4s^2$ (1.9%), and $[\text{Ar}]4d^2$ (1.6%). Since $4d$ and $7s$ orbitals are not included in the H^v reference space in order to maintain the quasidegeneracy of the valence orbital and enhance the perturbative convergence rate, this particular excited state (4^1S) is inaccurately described by the H^v method, and hence, is poorly estimated. Inclusion of $4d$, $4f$, $6p$, $7s$, and $7p$ orbital into the valence space will definitely improve the first-order description of the 4^1S excited state, but the perturbative convergence and the accuracy of high order MBPT (third order) may deteriorate due to the presence of a large number of intruder states, and a huge diagonal perturbation which exerts an opposing force to the perturbative convergence.

Table II compares the first few excitation energies obtained through a third-order H^v calculation with MCHF and CI values as well as experimental data. Like the binding energies, here we also find that all the low-lying excited states transition energies are in excellent agreement with experiment, while there exists a small but non-negligible error in the estimation of the high-lying states. We expect this trend from the binding-energy calculation as well as from previous H^v computation on Mg-like ions [7]. As explained above, it is the $4d$ and $7s$ orbitals whose absence in the valence orbital space inaccurately describes the 4^1S excited states and, hence, poorly estimates this transition energy. Likewise, the absence of $4d$, $4f$, $6p$, and $7p$ orbitals affects the computation of high-lying excited states for P , D , and F multiplets. For instance, it was shown in Ref. [22] that the major contribution to the 2^1D and 3^1D excited states comes from the CSF $[\text{Ar}]4s4d$, while the CSF $[\text{Ar}]4s4f$

TABLE II. Third-order H^v excitation energies (in rydberg) for S , P , D , and F multiplets of Ca I. $\Delta = |E_{\text{calc.}} - E_{\text{expt.}}|$.

Terms	State	Expt. ^a	δE ^b	δE ^c	$\delta E(H^v)$
<i>S</i> multiplets					
$4s^2$	1S	0.000	0.000	0.00000	0.00000
$4s5s$	3S	0.28741		0.01276	0.00646
$4s5s$	1S	0.30361	0.01289	0.01310	0.00807
$4s6s$	3S	0.36883		0.01447	0.00373
$4s6s$	1S	0.37079	0.01218	0.01239	0.00095
$4p^2$	1S	0.38078	0.00733	0.00702	0.03298
<i>P</i> multiplets					
$4s4p$	3P	0.13813		0.01489	0.00620
$4s4p$	1P	0.21553	0.00651	0.00655	0.00867
$4s5p$	3P	0.33305		0.01377	0.00421
$4s5p$	1P	0.33711	0.01398	0.01400	0.00638
$4p^2$	3P	0.35052		0.01808	0.01567
$3d^2$	3P	0.44231		0.02162	0.00266
$3d4p$	3P	0.35845		0.01018	0.01542
$3d4p$	1P	0.33472		0.05740	0.09362
<i>D</i> multiplets					
$3d4s$	3D	0.18543		0.02696	0.00600
$3d4s$	1D	0.19911	0.01155	0.01226	0.00407
$3d5s$	3D	0.43264			0.01491
$4p^2$	1D	0.37106			0.01176
$3d4p$	3D	0.34864			0.01770
$3d4p$	1D	0.32655			0.00464
<i>F</i> multiplets					
$3d4p$	3F	0.32637			0.00328
$3d4p$	1F	0.36941			0.04254
$3d^2$	3F	0.39630			0.00409

^aReference [30].

^bReference [22].

^cReference [23].

contributes about 80% to the 1^1F excited state. Since, we have not included these orbitals ($4d$, $4f$, and $7s$) in our reference space, the above-mentioned excited states, and so their state energies, are expected to be poorly described. We have also the estimated excitation energy for the $3d^2(^1G)$ state ($46\,422.8 \text{ cm}^{-1}$). There is no experimental data available for this, but our result is in fair agreement with the results of Brage and Fischer [24] ($46\,164.24 \text{ cm}^{-1}$) and Laughlin and Hansen ($46\,075.4 \text{ cm}^{-1}$).

Since a wide variety of reference spaces are used in the present calculation, it is important to study the low-order convergence behavior of the different choices. We have demonstrated the importance of the $3d$ orbital in the calculation. In Table III, we present the results obtained from typical $13V$ (defined below) third-order H^v computations where the computed transition energies are close to the experiment, but the relative order of the singlet and triplet excited states are incorrect.

As pointed out in Ref. [22], the low-lying excited S multiplet states of Ca I are dominated by the CSF's $[\text{Ar}]4sns$, and we construct a H^v reference space by allocating two

TABLE III. Transition energies (in rydberg) for S multiplets of Ca I, obtained from the third-order H^v method using the 13V ($4s, 5s, 6s, 7s, 4p, 5p, 6p$) valence space.

Terms	State	Expt.	H^v
$4s6s$	3S	0.36883	0.368218
$4s6s$	1S	0.37079	0.368004
$4s7s$	3S	0.40078	0.400079
$4s7s$	1S	0.40348	0.396437

active electrons of $4s$ orbital among $4s, 4p, 5s, 5p, 6s, 6p,$ and $7s$ (13V) orbitals. The computed third-order H^v transition energies are collected in Table III, and compared with experimental data. From Table III we find that $E_{2\ ^3S} > E_{3\ ^1S}$ and $E_{3\ ^3S} > E_{4\ ^1S}$ instead of $E_{2\ ^3S} < E_{3\ ^1S}$ and $E_{3\ ^3S} < E_{4\ ^1S}$. This incorrect ordering of the excited states of S multiplets most probably arises due to absence of the $3d$ orbital in valence space, because this peculiar problem does not arise in our 14V H^v calculation, where the $3d$ orbital is included in the valence space.

Effective dipole operator calculations have also been performed to compute the transition probability and the oscillator strengths of states. These calculations take the matrix element of the second-order effective dipole operator between the H^v eigenvectors as determined by the third-order calculations. While our estimated oscillator strengths and transition probabilities for ground to excited states (low lying) are reasonably close to the MCHF, CI, and experimental data, oscillator strengths for the excited to excited state transition are somewhat off (see Tables IV and V). The inferior

TABLE V. Transition probabilities (in 10^8 sec^{-1}) computed through the third H^v method for $S, P, D,$ and F multiplets of Ca I.

Transition	Multiplet	Wavelength	Expt. ^a	H^v
$4s^2 \rightarrow 4s4p$	$^1S - ^1P$	4227.9	2.18	2.011
$4s^2 \rightarrow 4s5p$	$^1S - ^1P$	2722.5	0.0027	0.022
$4s4p \rightarrow 4p^2$	$^1P - ^1S$	5514.5	1.1	2.64
$4s4p \rightarrow 4s5s$	$^3P - ^3S$	6123.9	0.354	1.452
$4s4p \rightarrow 4s6s$	$^3P - ^3S$	3958.2	0.175	0.392
$4s3d \rightarrow 4s5p$	$^3D - ^3P$	6163.1	0.19	0.698
$4s3d \rightarrow 4s5p$	$^1D - ^1P$	6717.7	0.12	0.102
$4s3d \rightarrow 4p3d$	$^3D - ^3P$	5271.7	0.50	1.758
$4s3d \rightarrow 4p3d$	$^3D - ^3D$	5596.0	0.49	0.886
$4s3d \rightarrow 4p3d$	$^3D - ^3F$	6465.6	0.53	0.348
$4s3d \rightarrow 4p3d$	$^1D - ^1P$	4526.9	0.41	1.923
$4s4p \rightarrow 4p^2$	$^3P - ^3P$	4303.7	1.36	1.586
$4s4p \rightarrow 4p^2$	$^1P - ^1D$	5859.1	0.66	0.353

^aCompiled in Ref. [31]. (The estimated uncertainty is $\approx 10\text{--}50\%$.)

quality of the oscillator strengths and probabilities for the ground to high-lying excited state and excited to excited state can be anticipated because the reference space lacks important configurations like $[\text{Ar}]4s7s, [\text{Ar}]4s4d,$ etc., that not only contribute to energies but also exert a strong influence on dipole properties [7]. (Note that oscillator strength and transition probability depends upon the transition energy and transition moment. Therefore, an error in the estimation of either of the two can yield a poor value for transition probability and oscillator strength.) The accuracy of the transition energies, oscillator strengths, and transition probabilities for

TABLE IV. Third-order H^v oscillator strengths for $S, P, D,$ and F multiplets of Ca I.

Transition	Multiplet	Wavelength	Expt. ^a	MCHF ^b	CI ^c	H^v
$4s^2 \rightarrow 4s4p$	$^1S - ^1P$	4227.9	1.75	1.89	1.820	1.74824
$4s^2 \rightarrow 4s5p$	$^1S - ^1P$	2722.5	0.0009	0.0174	0.00101	0.00734
$4s5s \rightarrow 4s5p$	$^1S - ^1P$	29288.1		0.9968	0.926	1.03968
$4s4p \rightarrow 4s5s$	$^1P - ^1S$	10346.6		0.3975	0.118	0.34376
$4s4p \rightarrow 4s6s$	$^1P - ^1S$	5869.2		0.0029	0.0009	0.07591
$4s5p \rightarrow 4s6s$	$^1P - ^1S$	25260.0		0.6567	0.168	0.93595
$4s4p \rightarrow 4p^2$	$^1P - ^1S$	5514.5	0.17	0.4449	0.120	0.25685
$4s5p \rightarrow 4p^2$	$^1P - ^1S$	19783.7		0.0211	0.0153	0.02999
$4s4p \rightarrow 4s5s$	$^3P - ^3S$	6123.9	0.121		0.156	0.4508
$4s4p \rightarrow 4s6s$	$^3P - ^3S$	3958.2	0.0248		0.187	0.0524
$4s3d \rightarrow 4s5p$	$^3D - ^3P$	6163.1	0.076		0.0407	0.030
$4s3d \rightarrow 4s4p$	$^1D - ^1P$	55473.3		0.0007	0.0014	0.00017
$4s3d \rightarrow 4s5p$	$^1D - ^1P$	6717.7	0.049	0.0916	0.0585	0.04237
$4s3d \rightarrow 4p3d$	$^3D - ^3P$	5271.7	0.15		0.201	0.46996
$4s3d \rightarrow 4p3d$	$^3D - ^3D$	5596.0	0.23		0.346	0.36092
$4s3d \rightarrow 4p3d$	$^3D - ^3F$	6465.6	0.42		0.364	0.29119
$4s3d \rightarrow 4p3d$	$^1D - ^1P$	4526.9	0.075		0.0585	0.28348
$4s3d \rightarrow 4p3d$	$^1D - ^1F$	5350.9		0.1087	0.0925	0.08844
$4s4p \rightarrow 4p^2$	$^3P - ^3P$	4303.7	0.377		0.529	0.4756
$4s4p \rightarrow 4p^2$	$^1P - ^1D$	5859.1	0.57	0.4706	0.550	0.31677
$4p^2 \rightarrow 3d4p$	$^1D - ^1F$			0.4998	0.00008	0.05281

^aCompiled in Ref. [31]. (The estimated uncertainty is $\approx 10\text{--}50\%$.)

^bReference [22].

^cReference [23].

TABLE VI. Variation of the third-order ground-state correlation energy (in a.u.) as a function of reference space.

Correlation contribution from	SR-MBPT	No. reference space orbitals		
		4V	10V	14V
Core-core	-0.27166	-0.27166	-0.27166	-0.27166
All electron	-0.33179	-0.32201	-0.31174	-0.30808
Core-valence + valence-valence	0.0	-0.05034	-0.04200	-0.03664

^aThe approximate contribution of the 4s valence orbital to the ground-state correlation energy is -0.060 128 a.u.

the ground to high-lying excited states and excited to excited states may be enhanced by including important CSF's in the reference space, and research in this direction is in progress.

We have seen that our result for the $\lambda = 6717.7 \text{ \AA}$ line [i.e., the $4s3d (^1D)$ to $4s5p (^1P)$ transition] is in good agreement with the experimental values for both the excitation energy and the transition dipole moment. Thus the observed crude abundances of neutral calcium [2] most probably arise because of some other property of the Am binaries which is presently not understood.

Table VI displays the contribution to the correlation energy arising from the core-core, core-valence, valence-valence, and all-electron interactions. Unlike the core-core correlation energy computation, it is not straightforward in our MR-MBPT approach to separate out the core-valence and valence-valence contributions, and we therefore only quote the sum total of those two contributions which can also be obtained by subtracting the core-core contribution from the all-electron correlation energy. It is evident from Table VI that the core-valence and valence-valence correlation contributions decrease with the increasing dimension of the reference space. This variation in the correlation energy (core-valence plus valence-valence contributions) is simply a consequence of the imposition of the valence orbital degeneracy condition. It can easily be shown that the forced valence orbital degeneracy condition enlarges the gap between the core and valence orbital energies which increases with the increasing size of the nondegenerate reference space [21,28]. Consequently, the correlation contribution from core-valence and valence-valence interactions decreases with increasing size of the reference space.

It has been observed that the second-order H^v computations often overestimate or underestimate the state energies, and this eventually is counterbalanced by the third-order H^v contributions. Thus the low-order perturbative convergence of the H^v method sometimes exhibits an oscillatory pattern that arises mainly because of the valence orbital energy averaging procedure, especially when the zeroth-order orbital eigenspectrum is highly nonquasidegenerate. For example, the error in the computed $4s \rightarrow 4p$ resonant transition energy rapidly drops from 35% to 2.5% as the perturbation order increases from 1 to 3. However, for a nonresonant transition the perturbative convergence shows a somewhat oscillatory behavior. This type of convergence pattern is quite common, and has also been observed in earlier calculations where the triplet state is described more accurately than the singlet state with a minimal reference space H^v computation. A systematic increase of the valence space, for instance, the inclusion of 3d and 6s orbitals into the reference, improves the low-

order perturbative convergence of the H^v method, and this way reduces the error in the computed third-order excitation energy from 8.5% to 3.5% for a resonant transition and from 10.7% to 3.17% for a nonresonant transition without sacrificing the second-order accuracy of transition energy, which is small compared to the above. The inclusion of the 3d and 6s orbitals not only improves the accuracy of H^v transition energies, but also improves the oscillator strengths.

We reiterate that the use of a large valence space may provide a very good first-order description of the excited states of interests, but eventually it may destroy the perturbative convergence because it involves a trade-off. The success of the H^v method largely depends upon the relative importance of the competing factors. The large reference space provides a better first order description of the state of interest, and, thereby, accelerates the convergence rate, while the diagonal perturbation that rises from the orbital averaging procedure destroys the perturbative convergence. Thus care should taken during the selection of the reference space. In fact, the success of the H^v scheme lies largely in the appropriate selection of the valence space, a process that requires some trial and searching and an *a priori* knowledge of the most important configurations.

V. CONCLUSION

The effective shell Hamiltonian method is applied to compute the excitation energies and oscillator strengths for Ca I. The accuracy of the computed low-lying (and some high-lying) excited-state energies, binding energies, oscillator strengths, and first ionization potential demonstrate the power of the method. The accuracy of the computed properties through the H^v method are in good agreement with the other correlated theoretical calculations and experimental data. This work highlights a number of unique and desirable features of the H^v method. For instance, H^v calculations provide a uniform accuracy for more excited states than is obtained with some other schemes, such as the MCHF and CI methods.

The present calculations suggest that a minimal reference space is sufficient for an accurate estimation of the excitation energies of the triplet states, while a large reference space is necessary to treat the singlet states. Since our computations have covered a wide range of reference spaces, it might be possible to use different set of reference spaces for excited states of different symmetries. This kind of approach has been found to be quite successful in generating potential-energy surfaces [26].

On the whole the H^v method improves the agreement

between theory and experiment, but a number of problems still remain. It has been argued over the past few years that ever present intruder states can affect the numerical stability of the large-scale H^v calculations. However, this assumption has been dispelled by extensive studies of the convergence behavior [26–28]. It should be emphasized that a large (complete) reference invariably leads to the situation where the zeroth-order eigenspectrum of the reference space overlaps with that of the virtual space states, i.e., the large (complete) reference space MR-MBPT computations must ultimately

become plagued by the intruder states, and, consequently yield divergent perturbative expansion. However, when pursuing a large-scale low-order perturbative computation, we generally neither know nor care whether the series is truly convergent or not, since this information has no practical value. The H^v approach uses physical and mathematical considerations to produce acceptable accurate results in low order. The present computations for neutral calcium reinforces our prior assertions that this method can be used as a useful alternative scheme for the calculations of atomic and molecular properties.

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