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Application of the effective valence shell Hamiltonian method to accurate estimation of oscillator strengths and excitation energies of Mg-like ions

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The *ab initio* effective valence shell Hamiltonian (H^v) method is used to compute the excitation energies and oscillator strengths for resonance transitions in Mg-like ions, as well as their lowest ionization potentials. The computed excitation energies and oscillator strengths from the H^v method are in excellent agreement with experiment and with the best values from other high level correlated computations, where available. Several previous discrepancies between theory and experiment are now removed. The present work also investigates the dependence of the calculated H^v oscillator strengths on the nature and choice of the valence orbitals and provides a comprehensive study of the convergence of H^v calculations with respect to the enlargement of the valence space. © *1998 American Institute of Physics.* [S0021-9606(98)03006-2]

I. INTRODUCTION

Electronic structure theory plays a unique role in understanding atomic and molecular processes and spectroscopic observations of astrophysical interest. For instance, an accurate knowledge of excitation energies and oscillator strengths may be used to infer the molecular abundances, temperatures, etc., in celestial objects. The laboratory preparation or creation of highly reactive astrophysically important species, such as free radicals or highly stripped ions, is often extremely difficult, and so too is the study of their important atomic and molecular processes. In these circumstances, electronic structure calculations provide essential data for the interpretation of astrophysical observations. Even when the species can be replicated in the laboratory, theory often provides crucial, otherwise experimentally inaccessible, additional information concerning the system.

Comparisons between theoretical predictions and experiment continue to provide a strong driving force toward developing improved electronic structure theories which are now at a stage where explanations and accurate predictions are possible for many critical physical phenomena. Although these theories have matured considerably, the accurate estimation of excited state properties (both atomic and molecular) and transition dipole moments, oscillator strengths, etc., remains a major challenge. The present limitations on the accuracy of excited state computations arise mainly due to (1) the use of inadequate basis sets that often fail in properly describing the character of the excited states and (2) an unbalanced treatment of dynamical correlation and polarization effects. The accuracy of the computed excitation energy depends largely upon the quality of the unoccupied valence orbitals into which the excitation occurs. Therefore, an appropriate description of these unoccupied valence orbitals is also one essential ingredient for obtaining the desired accuracy for excited state properties. The stringent requirements on the unoccupied orbitals necessitate the use of a suitable basis set, and this is generally accomplished, in part, by increasing the basis set size through the addition of several polarization and diffuse functions.

While problems due to basis set inadequacy can be removed partially by enlarging the basis for small and moderate sized atomic and molecular systems, the proper treatment of electron correlation requires rigorous size-extensive theories. The maintenance of size-extensivity[1] is now considered to be crucial in computing energy differences and potential energy surfaces, especially near regions of bond breaking or avoided (or real) crossings between potential energy surfaces. Effectively, the size-extensivity requirement translates into a need for properly treating the differential correlation energies of the interacting (or initial and final) zeroth order states, such that the state energies rigorously scale linearly with the number of electrons. The size-extensivity condition is violated by many popular excited state electronic structure theories, such as configuration interaction with only single (CIS), single and double (CISD), etc., excitations.

Widely used electronic structure theories for excited state computations can be classified broadly into two categories: (a) transition based methods which provide energy differences directly, and (b) state-based methods which yield individual state energies. The first category includes approaches, such as the random phase approximation (RPA)[2] and coupled-cluster based linear response theory (CCLRT),[3–8] whereas the self-consistent field (SCF), configuration interaction (CI), many-body perturbation (MBPT) theories,[9–23] or the Tamm–Dancoff approximation (TDA), are state-based approaches. The RPA scheme has been found to be quite useful for many atomic and molecular systems, but the method often suffers from numerical instabilities, as evidenced by the emergence of imaginary excitation energies.[24] The linear response approach is a very powerful correlated method that is closely related to state-based multireference coupled-cluster (MRCC) methods (see Refs. 25–28 for a comprehensive review). Provided the coupled-cluster (CC) equations are stable for the ground state, the matrix eigenvalue nature of the coupled-cluster based linear response (CCLRT) method eliminates the numerical instability problems introduced by the so-called *intruder states*,[29,30] which are virtual space states that become degenerate with reference space states for complex values of a perturbation parameter (within the unit circle), thereby spoiling the perturbative convergence of the wave operator equations.[31–33] Therefore, the accuracy of excitation energies available from this CCLRT method directly depends upon the success of the CC computations for the ground electronic state. In addition, the calculation of excitation energies and transition moments with the linear response theory involves the diagonalization of a large (nonsymmetric) matrix whose dimension is either equal (for singlet states) or greater (for triplet states) than the dimension of the CC equations necessary for accurately treating the ground state (at the CCSD level). Thus, the approach is numerically efficient only for small to moderately sized atomic and molecular systems.

The effective valence shell Hamiltonian method (H^v)[34–48] does not suffer from many of the above limitations, although this scheme may encounter a convergence problem due to the presence of intruder states. However, the intruder state problems can often be removed or, at least, strongly mitigated by applying several physically and mathematically motivated methodological techniques.[31–33,45] Some conceptual advantages of the effective valence shell Hamiltonian method are the following: (i) A common set of orbitals is used to describe all the states of interest. This choice cancels common correlation energy contributions for all the states and enables the inclusion of all correlation and polarization contributions to the transition moments. (ii) The method provides a very balanced description of all the states in a one-shot procedure. (iii) The H^v approach manifestly maintains the size-extensivity of the computed state energies (the roots of the effective Hamiltonian.) (iv) A single computation of the effective Hamiltonian provides all the ionization potentials, electron affinities, and excitation energies. (v) The method is not burdened by the large matrix dimensionality problem because the effective Hamiltonian operates only on the reference space states (generated by allocating valence electrons among the valence orbitals in all possible ways), whose number is usually quite small, involving no more than several hundred states.

While the original motivation for developing the effective valence shell Hamiltonian theory has been to understand the underlying approximations of semiempirical electronic structure methods and to devise improved *ab initio* semiempirical electronic structure procedures, it is now widely appreciated that the method is capable of generating reliable potential energy surface for the ground and excited states, excitation energies, ionization energies, and bond cleavage energies, as well as molecular properties such transition dipole moments and oscillator strengths.[40,43,46–48] Several papers document the H^v formalism, the computational algorithms for evaluating atomic and molecular properties, and the convergence behavior.[31–33] Despite the recent tremendous successes of the H^v method for accurately assigning the electronic spectrum of complex molecular systems, such as conjugated polyenes and inorganic molecules, only rather older, small basis set applications have been made for atomic systems.[35–37]

The present work considers four astrophysically important atomic systems, the isoelectronic series Mg, Al^{+}, Si^{+2}, and P^{+3}. Extensive theoretical[49–56] and experimental[57–61] studies of the excitation energies and oscillator strengths for these four atomic systems are available employing a wide variety of techniques. Nevertheless, considerable discrepancies continue to exist between the theoretically computed oscillator strengths (and excitation energies) and experiment, and the magnitude of the discrepancies grows with increasing nuclear charge. For example, earlier large discrepancies in Hartree–Fock[50] computations for the oscillator strengths of the Mg resonant transition have been shown by Fischer[51] to arise mainly from the omission of intervalence correlation effects in the Hartree–Fock procedure. In fact, Fischer's multiconfiguration Hartree–Fock (MCHF) calculations for Mg are quite close to experiment and to other nonrelativistic methods.[49,56] However, similar disagreements for the excitation energies and oscillator strengths also persist for the Al^{+}, Si^{+2}, and P^{+3} systems.[62–69]

This paper describes large scale H^v computations that eliminate these prior discrepancies between theory and experiment. The present work again demonstrates that the H^v scheme not only produces highly accurate excitation energies but also a precise estimation of the oscillator strengths. In accord with our excellent representation of the low-lying excited states, the accuracy of our computed high-lying excited state energies (not described by the other *ab initio* works) is also uniform. We further document the importance of various types of electron correlation in the computation of excitation energies and transition moments.

Section II begins with a brief review of the H^v method for computing the energy and other properties, such as the dipole and transition moments. The computed results and discussion are presented in Secs. III and IV, respectively.

II. THEORY

Perturbation theory decomposes the molecular electronic Hamiltonian H into a zeroth order part H_0 and a perturbation V,

$$H = H_0 + V, \tag{2.1}$$

where H_0 is constructed as a sum of one-electron Fock operators. The full many-electron Hilbert space is then partitioned into a primary space (also called the model or reference space) with projector P and its orthogonal complement with projector $Q = 1 - P$. The P space spans the valence space of all distinct configuration state functions involving a filled core, and the remaining electrons are distributed among the valence orbitals in all possible ways to ensure completeness of the P-space. Hence, the Q-space contains all basis functions with at least one core hole and/or one occupied excited orbital. The H^v method transforms the full Schrödinger equation,

$$H\Psi_i = E\Psi_i, \tag{2.2}$$

into the P-space effective valence-shell Schrödinger equation,

$$H^v\Psi_i^v = E\Psi_i^v, \tag{2.3}$$

where the valence space eigenfunctions $\Psi_i^v = P\Psi_i$ are the projections of the exact eigenfunctions and the energies E are the corresponding exact eigenvalues of the full Schrödinger equation. The H^v method provides the unique second order approximation,

$$H^v = PHP + \tfrac{1}{2}\sum_{\Lambda,\Lambda'} [P(\Lambda)VQ(E_\Lambda - H_0)^{-1}QVP(\Lambda') + h.c.], \tag{2.4}$$

where $h.c.$ designates the Hermitian conjugate of the preceding term and $P(\Lambda)$ designates the projector onto the valence space basis function $|\Lambda\rangle$.

In order to compute the diagonal and off-diagonal matrix elements of an operator A between the normalized full space wave functions Ψ_i within H^v theory, the matrix elements $\langle\Psi_i|A|\Psi_i'\rangle$ are transformed into an effective valence-shell operator A^v between the orthonormal valence space eigenfunctions Ψ_i^v, i.e.,

$$\langle\Psi_i|A|\Psi_i'\rangle = \langle\Psi_i^v|A^v|\Psi_i'^v\rangle. \tag{2.5}$$

The effective operator A^v can likewise be expanded as

$$A^v = PAP + \tfrac{1}{2}\sum_{\Lambda,\Lambda'} [P(\Lambda)VQ(E_\Lambda - H_0)^{-1}QAP(\Lambda') + h.c]. \tag{2.6}$$

Thus, the expectation values and off-diagonal couplings may be determined by first solving Eq. (2.3) and then by taking the corresponding matrix elements on the right-hand side of Eq. (2.5). Once A^v is evaluated, it furnishes all diagonal and off-diagonal matrix elements within the P-space states.

Many-body theory techniques can be applied to reduce Eq. (2.6) and express the matrix elements of A^v directly in the valence orbital basis. The resulting equations are available elsewhere[35] in terms of core-, one-, two-,... electron valence shell operators A_c^v, A_i^v, $A_{ij}^v, \ldots$, respectively, in the operator representation,

$$A^v = A_c^v + \sum_i A_i^v + \tfrac{1}{2}\sum_{i,j} A_{ij}^v + \cdots, \tag{2.7}$$

where A_c^v is the constant core contribution, and A_i^v is a one-electron effective operator with matrix elements $(v|A_i^v|v')$ in the valence orbital basis. When A is the dipole operator, the effective dipole operator A^v acts only on the P-space, i.e., valence space. Although the dipole operator is a one-electron operator, two-electron effective operators A_{ij}^v appear in the lowest order nontrivial correction from the perturbation expansion in Eq. (2.6). This nonclassical two-electron term is necessary to provide accurate dipole and transition moments. In actual computations, the effective Hamiltonian H^v is first diagonalized to obtain desired eigenvalues and eigenfunctions Ψ_i^v. The latter are then employed along with Eq. (2.5) to compute expectation values and transition moments of the operator A by use of the effective valence-shell operator A^v.

III. RESULTS AND DISCUSSION

We employ the uncontracted $11s7p$ Gaussian basis of Dunning and Hay, augmented by three d-functions (four for P^{3+}) and one s and two p diffuse functions for Mg, Al^+, Si^{2+}, and P^{3+}. The total number of basis functions used for the H^v computations ranges from 57 (for Mg) to 63 (for P^{3+}). Three sets of reference spaces (two for P^{3+}) are employed to investigate the dependence of the computed H^v oscillator strengths and excitation energies on the choice of valence space. The valence orbitals are selected based on their orbital energies (to avoid or minimize near degeneracies between the reference and virtual space states) and on their relative importance in properly describing the excited states of interest, i.e., in providing a high quality first order approximation from the *PHP* term in Eq. (2.4) to minimize the required perturbative corrections. The reference space obviously must include the $3s$ (highest occupied orbital) and the $3p$ (lowest unoccupied orbital) for describing the $(3s)\ {}^1S_0 \rightarrow (3s3p)\ {}^1P_1$ transition. Thus, our smallest reference space contains only the $3s$ and $3p$ orbitals with two active electrons (called the $4V$ reference space). Since a minimal $\{3s,3p\}$ reference space is not adequate for providing a highly accurate description of the singlet excited states,[48] the addition of $3d$ and $4s$ orbitals provides the second reference space (called the $10V$ reference space). The anticipated importance of the $3d$ orbitals stems not only from their quasidegeneracy with the $3p$ orbitals but also from their non-negligible contribution to the ${}^1P_1$ excited states. In addition, the $|(\mathrm{core})^{10}3d^2\rangle$ reference space configuration state function (CSF) mixes with the zeroth order ground state $|(\mathrm{core})^{10}3s^2\rangle$ CSF and thereby stabilizes the ground state energy. Therefore, energetic considerations appear to render the $\{3s,3p,3d,4s\}$ reference space as optimal. However, the $|(\mathrm{core})^{10}3s4p\rangle$ virtual space CSF is more important for describing the ${}^1P_1$ state than the reference space $|(\mathrm{core})^{10}3p3d\rangle$ CSF (for the $\{3s,3p,3d\}$ valence orbital space) because the $|(\mathrm{core})^{10}3p3d\rangle$ CSF is doubly excited and, hence, weakly coupled to the $|(\mathrm{core})^{10}3s3p\rangle$ CSF (the dominant CSF for the ${}^1P_1$ excited state). Therefore, inclusion of the $|(\mathrm{core})^{10}3s4p\rangle$ CSF into the reference space might be expected to improve the first order approximation and hence the perturbative convergence of the H^v method. Although the $|(\mathrm{core})^{10}3p3d\rangle$ CSF is less important for the ${}^1P_1$ state, its presence in the reference space is useful to help avoid ''intruder state'' type numerical instabilities in the H^v perturbative expansions. [Since the $|(\mathrm{core})^{10}3p3d\rangle$ CSF is energetically lower than the $|(\mathrm{core})^{10}3s4p\rangle$ CSF (in zeroth order), the $|(\mathrm{core})^{10}3p3d\rangle$ CSF would act as an intruder state unless it is included in the reference space.] The above arguments also apply to the $4s$ orbital and, hence, it is also included in the largest valence orbital space. Generally, H^v computations avoid the use of very large non-

TABLE I. Excitation energies (in cm^{-1}) for resonant transitions in Mg-like ions.

State	Dominant configuration	H^v 4V	10V	13V	Experiment[a]
Mg					
$^3P_2$	$3s3p$	21 102.46	21 460.89	21 057.52	21 911.14
$^1P_1$	$3s3p$	35 333.69	33 758.99	34 898.95	35 051.36
$^3S_1$	$3s4s$		42 471.33	41 840.89	41 197.37
$^1S_0$	$3s4s$		43 981.99	44 030.92	43 503.00
$^1D_2$	$3s3d$		47 009.20	46 298.23	46 403.14
$^3D_3$	$3s3d$		48 763.60	48 045.09	47 957.04
Al$^+$					
$^3P_2$	$3s3p$	37 420.15	36 527.23	36 949.83	37 579.30
$^1P_1$	$3s3p$	60 075.94	59 550.49	59 913.70	59 849.70
$^1D_2$	$3p^2$		85 060.44	85 521.62	85 479.00
$^3S_1$	$3s4s$		89 350.12	89 786.70	91 271.20
$^1S_0$	$3s4s$		93 317.32	93 897.88	95 348.20
Si^{2+}					
$^3P_2$	$3s3p$	52 133.00	51 363.96	51 782.51	53 019.00
$^1P_1$	$3s3p$	83 217.49	83 041.35	83 245.45	82 885.00
$^1D_2$	$3p^2$		121 112.72	121 601.48	121 946.00
$^1S_0$	$3p^2$		153 253.05	153 359.29	153 443.00
P^{3+}					
$^3P_2$	$3s3p$	67 170.08		66 661.71	68 607.40
$^1P_1$	$3s3p$	105 913.55		106 110.39	105 189.90
$^1D_2$	$3s3d$			158 322.17	158 138.20
$^1D_2$	$3p^2$	168 301.75		163 880.76	166 144.00
$^3D_3$	$3s3d$			198 484.15	189 389.00
$^1S_0$	$3p^2$	197 830.10		195 836.70	194 588.50
$^3S_1$	$3s4s$			224 393.11	226 888.60
$^1S_0$	$3s4s$			231 539.56	233 995.00

[a] See Ref. 70.

quasidegenerate reference spaces (a) because an enlarged non-quasidegenerate reference space introduces a huge diagonal perturbation (arising due to the imposition of degeneracy upon the zeroth order reference space) which can destroy the perturbative convergence, and (b) because an extended reference space greatly increases the computational labor due to the presence of a large number of valence orbitals in the reference space. However, the addition of the $4p$ orbitals to the second set of reference spaces ($\{3s,3p,3d,4s\}$) provides an improved first order description of the $^1P_1$ excited state because both $3d$ and $4p$ orbitals yield important contributions. Thus, our consideration of the three different reference spaces further investigates the tradeoff between the desire for accurate first order approximations (from large reference spaces) and the requirements of quasidegeneracy (provided by small reference spaces).

Tables I and II compare the H^v excitation energies of Mg-like ions with experiment[70] and with other theoretical calculations. Apart from a few exceptions, our estimated excitation energies are reasonably close to experiment (see Table I) and are more accurate than those from previous configuration interaction (CI) calculations[53] and RRPA (relativistic random phase approximation) computations.[52] On average, the H^v results are as good as the MC-RRPA (multiconfiguration RRPA) calculations of Chou *et al.* (see Table II). (The MC-RRPA calculations without core excitations are, however, less accurate than the H^v results.) The excited singlet states are more accurately treated by the H^v method than the excited triplet states, but the discrepancy decreases with diminishing size of the reference space, a feature which has also been found and explained in our previous H^v computations for π-electron systems.[48] Energetic considerations are given above to motivate the choice of the 10V-reference space ($\{3s,3p,3d,4s\}$) as appropriate, and, hence, this reference space is expected to provide an accurate estimate of the excitation energies. Although the 10 orbital (10V) reference space computations yield a fairly accurate description of the excited states, the results deviate more from experiment than the 4- and 13- orbital valence reference space computations (from the $\{3s,3p\}$ and $\{3s,3p,3d,4s,4p\}$ reference spaces, respectively). A plausible explanation for the lower accuracy of the 10V space calculations is the following: Addition of the $4s$ and $3d$ orbitals into the reference space improves the first order description [from the *PHP* term in Eq. (2.4)] for both the ground and excited states of the Mg-like ions, but it also introduces a large diagonal perturbation upon imposition of the valence orbital degeneracy condition. While a better first order representation of the reference space states (achieved via the inclusion of additional valence orbitals) contributes to an acceleration of the perturbative convergence, the large diagonal perturbation appears to exert a more negative influence on the perturbative convergence. This behavior reflects the tradeoff in the H^v scheme between desiring large reference spaces and requiring these spaces to be quasidegenerate. The success of the H^v method largely depends upon balancing these two opposing factors. That is, the H^v approach succeeds only when the effect of the diag-

TABLE II. Comparison of H^v excitation energies (in cm^{-1}) and oscillator strengths for $(3s^2)\ ^1S_0\rightarrow(3s3p)\ ^1P_1$ transition in Mg-like ions with other many-body methods.

	CI[a]	RRPA[b]	MCHF[c]	MC-RRPA[d] I[e]	II[f]	H^v 4V	10V	13V	Experiment[g]
Mg		32 833	35 292			35 333.69	33 758.99	34 898.95	35 051.36
Al$^+$	60 342.0	58 534	61 222	60 169	59 427	60 075.94	59 550.49	59 913.70	59 849.70
Si^{2+}		82 193	80 607	83 686	82 564	83 217.49	83 041.35	83 245.45	82 883.00
P^{3+}		104 952	107 323	106 537	105 124	105 913.55		106 110.39	105 189.90
Av. error		1115.49	1505.51	823.13	269.20	391.68		374.84	

[a] See Ref. 53.
[b] Cited in Ref. 55.
[c] See Ref. 55.
[d] See Ref. 62.
[e] Without core excitations.
[f] With core excitations.
[g] See Ref. 70.

TABLE III. Oscillator strengths for resonance transition in Mg-like ions.

				MC-RRPA[c]		H^v			
	MCHF[a]	CI	RRPA[b]	I[d]	II[e]	$4V$	$10V$	$13V$	Experiment
Mg	1.71					2.18	1.97	2.00	1.81[j]
Al^+		1.87[f]	1.85	1.83	1.78	1.95	1.78	1.82	1.8±0.3[k] 1.9±0.6[l] 1.84±0.12[j]
Si^{2+}		1.63[g]	1.73	1.70	1.65	1.76	1.66	1.68	1.7±0.4[l] 1.6±0.2[m]
P^{3+}		1.48[h]	1.59	1.57	1.52	1.61		1.56	1.8±0.2[n] 1.6±0.16[i]

[a] See Ref. 50.
[b] See Ref. 52.
[c] See Ref. 62.
[d] Without core excitations.
[e] With core excitations.
[f] See Ref. 53.
[g] See Ref. 63.
[h] See Ref. 64.
[i] See Ref. 65.
[j] See Ref. 66.
[k] See Ref. 67.
[l] See Ref. 68.
[m] See Ref. 69.
[n] See Ref. 58.

TABLE IV. Transition moments for resonance transition in Mg-like ions.

	H^v		
	$4V$	$10V$	$13V$
Mg	2.603	2.533	2.505
Al^+	1.889	1.813	1.824
Si^{2+}	1.522	1.479	1.489
P^{3+}	1.291		1.270

onal perturbation is less important. In the $10V$-reference space computation, the $|(\text{core})^{10}3p3d\rangle$ reference space CSF is a doubly excited state (with respect to the ground state) which is weakly coupled to the $|(\text{core})^{10}3s3p\rangle$ CSF (the most important reference space CSF for the excited $^1P_1$ state). Therefore, this CSF provides a very small contribution to $^1P_1$ state. On the other hand, since the $3d$ orbital (also the $4s$) is rather high lying compared to the other valence orbitals, its inclusion into the reference space produces a large diagonal perturbation, thereby introducing a stronger convergence retarding factor than the insignificant improvement it produces in the first order description. The above mentioned opposing factors do not appear in the four-valence orbital ($\{3s,3p\}$) reference space H^v computations, which, therefore, yield the anticipated good results. Continuing these arguments leads to the expectation that the 13 valence orbital H^v computations would be even less accurate than the 10 valence orbital H^v computation. However, the 13 valence orbital ($\{3s,3p,3d,4s,4p\}$) reference space includes all the dominant and the next level subdominant CSFs in the reference space, thereby successfully overcoming any impediment to convergence difficulties induced by the diagonal perturbation. In fact, the 13 valence orbital H^v computation provides a precise estimate of the excitation energy of the $^1P_1$ state in addition to that of other high-lying excited states.

While the four-valence orbital reference space H^v computations successfully describe the excited state energies of interest, they yield relatively poor oscillator strengths (see Table III), a feature which is, of course, undesirable because a reliable theoretical method should treat both accurately. A more detailed analysis indicates that the main error of the four-valence orbital reference space computation lies in an overestimation of the transition moment (see Table IV) and, hence, the oscillator strength (which is proportional to the square of the transition moment). The inferior quality of the oscillator strengths from the minimal reference space computations can be anticipated because the reference space lacks important configurations like the $|(\text{core})^{10}3p3d\rangle$ and $|(\text{core})^{10}3s4p\rangle$ CSFs that contribute very little to the energies but exert a stronger influence on dipole properties. The 13-valence orbital H^v computations are the most consistent and balanced among those from the three sets of valence spaces. Further support for this conclusion stems from a comparison of the computed ionization potentials with experiment in Table V.

Since a wide variety of reference spaces are used in the present calculations, it is necessary to study the low order convergence behavior of the different choices. The Mg atom provides a useful illustration of the general behavior for the other cases. At this juncture, we note the trend that the second order H^v computations often overestimate/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 mainly arises due to the valence orbital energy averaging procedure, especially when the zeroth order orbital eigenspectrum is highly non-quasidegenerate. We first analyze the perturbative convergence of our smallest reference space ($4V$) calculations. The error in the computed $3s\rightarrow 3p$ resonant transition energy rapidly drops from 25%→0.8% as the perturbation order increases from 1→3. While the computed excitation energy for the resonant transition displays a uniform convergence pattern, the perturbative convergence for the nonresonant transition is somewhat oscillatory, where the error in the computed excitation energy is only 0.6% at second order as compared to 5% and 3.5% at first and third order, respectively. This type of convergence pattern is quite common and has also been found elsewhere[48] where the triplet state is described more accurately than the singlet state with a minimal valence space H^v computation.

A systematic increase in the reference space significantly improves the low order perturbative convergence of the H^v scheme by introducing more nondynamical correlation contributions. For example, inclusion of the $3d$ orbitals in the reference space (in addition to the $3s$ and $3p$), reduces the

TABLE V. Ionization potentials (in eV) in Mg sequence.

	H^v			
Ions	$4V$	$10V$	$13V$	Experiment[a]
$Mg\rightarrow Mg^+ + e$	7.539	7.637	7.555	7.645
$Al^+\rightarrow Al^{2+} + e$	18.645	18.532	18.596	18.823
$Si^{2+}\rightarrow Si^{3+} + e$	33.248	33.135	33.220	33.460
$P^{3+}\rightarrow P^{4+} + e$	51.088		51.023	51.354

[a] See Ref. 70.

error in the computed third order excitation energy from 3.5% to 1.8% at third order for the nonresonant transition without sacrificing the accuracy of the second order nonresonant transition energy (off by 0.8%). Inclusion of the $3d$ orbitals in the reference space also improves the low order convergence for the resonant $3s \rightarrow 3p$ transition of the Mg atom, where the accuracy of the first order H^v calculation decreases from 5% to 1.8%. The quality of the H^v computation further improves when the $4s$ and $4p$ orbitals are included in the reference space. In this case, the resonant (nonresonant) $3s \rightarrow 3p$ transition energies are off by 9.6% (2.5%), 2.4% (3.5%), and 0.4% (3.7%) from the first, second, and third order H^v computations, respectively. A similar trend is also exhibited for the high-lying excited states, as well as for calculations with smaller basis sets. [Three additional sets of H^v calculations have been performed for the Mg atom with different numbers (33, 49, and 90) of basis functions by deleting/adding s, p, d, f, and g functions from/to the original basis set (with 57 functions). The perturbative convergence of computed excitation energies for these three sets of calculations behaves exactly as expected. In particular, the accuracy generally increases with the size of basis.] The above trends displayed by the H^v computations indicate that this method quite accurately includes the differential interstate correlation energies.

Although the H^v method is primarily designed to produce accurate differences in correlation energies (not necessarily the individual state energies) as evidenced by a large number of previous H^v calculations, it nevertheless is pertinent to analyze the fraction of ground state correlation energy recovered with different basis sets and reference spaces. The Gaussian basis sets employed here are not designed for optimal recovery of the full correlation energy of atoms unless the basis is very large (complete) and appropriate. Hence, we do not anticipate obtaining a large portion of the ground state correlation energy, but the computations should definitely approach the exact value with increasing size of the basis set. The present computation shows that the ground state correlation energy (third order) increases from -0.1618 to -0.2458 a.u. as the basis set increases from 33 to 90 functions. (The nonrelativistic ground state correlation energy is estimated by Clementi and Veillard[71] as -0.428 a.u.) Inclusion of more basis functions or the use of Slater functions should help to recover more of the correlation energy. However, as evidenced by computations with various basis sets, the transition energies and oscillator strengths are expected to be very slightly changed in this process, and it is the accurate treatment of the transition energies and oscillator strengths that forms the prime focus of resolving previous discrepancies with experiment.

IV. CONCLUSION

Vertical excitation energies, ionization potentials, and oscillator strengths of Mg-like ions are calculated using the effective valence shell Hamiltonian method. Both low-lying (and even some high-lying) excitation energies and oscillator strengths are in good agreement with experiment and with the most accurate highly correlated theoretical calculations. The present calculations highlight a number of unique and desirable features of the H^v method. For example, the H^v computations provide a more uniform accuracy for most excited states than is obtained with some other schemes, such as the MCHF,[55] CI,[53] and RRPA[52] methods. [Table II provides the average deviation between the calculated and observed $(3s^2)\ ^1S_0 \rightarrow (3s3p)\ ^1P_1$ transition energies for the Al^+, Si^{2+}, and P^{3+} ions.] The present H^v computations concur with previous observations, indicating that while a large reference space is necessary for the accurate estimation of excitation energies to the singlet excited states, a minimal reference space suffices for treating the triplet state. This observation is readily understood based on the more diffuse character of the low-lying excited singlet states than their isoconfigurational triplet counterparts. Our use of individualized reference spaces for different groups of excited states is in accordance with the common usage of multiple reference spaces in other many-body methods, a procedure that becomes advantageous because of the different nature of correlation in various classes of excited states. The greater importance of polarization contributions to transition moments than to excitation energies is reflected here in the need for larger reference spaces to provide transition moments of comparable quality to the excitation energies available from calculations with smaller reference spaces. This situation complies with the larger basis set requirements for accurate dipole properties than energies.

It has been argued that large scale H^v computations are highly vulnerable to numerical instabilities from the allegedly always present serious intruder state problems. However, our extensive studies on the convergence behavior of the H^v method dispels this assumption.[31–33] The proper choice of the valence orbitals and reference space plays a significant role in all multireference many-body theories, and the H^v method is no exception. It should be emphasized that a large (complete) reference space invariably leads to situations where the zeroth order eigenspectrum of the P space states overlaps with that of the Q space states, i.e., large (complete) reference space MR-MBPT computations must ultimately become plagued by intruder states and, consequently, frequently yield divergent perturbative expansion. However, when pursuing large scale perturbative computations, we generally neither know nor care whether the series actually converges, since this information is of little practical value for computations truncated at low orders. Mathematical convergence depends upon the behavior of the indefinitely high order terms which are generally unavailable for large scale computations. Moreover, if a truly convergent perturbative series fails to provide accurate low order predictions, the method has no practical value. On the contrary, a formally divergent but asymptotic series is very useful if it reliably provides low order results as does the H^v method. The H^v approach uses a combination of physical and mathematical considerations to produce accurate results in third order. The high accuracy of the present computations for the Mg sequence strongly supports these claims.

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