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Test of a Multi-Reference Many-Body Perturbation Theory for the Description of Electron Correlations in four Valence Electron States of Transition Metal Atoms

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Received March 3, 1986

A multi-reference many-body perturbation theory (MRMBPT) method is critically tested in second order by comparing with the corresponding configuration interaction (CI) calculations. Excitation energies of the four-valence-electron states of transition metal atoms and ions are used for the comparison. The agreement between the second order MRMBPT and CI calculations is very reasonable, confirming the reliability of the second order MRMBPT method. The reliability of calculations with the present second order MRMBPT method was only been inferred empirically in the past since most results have been gauged by the agreement with experiment and/or with other MRMBPT calculations based upon different sets of orbitals and configuration spaces. The present MRMBPT method appears to be an efficient ab initio multi-reference method for the calculation of electron correlation effects in atoms and molecules, and it is shown how MRMBPT can be used to estimate core-core and core-valence correlation effects which are often omitted in CI calculations because too many configurations and correlating electrons are involved.

Introduction

Many-body perturbation theory (MBPT) is one of the com-

mon techniques for the study of electron correlation, an effect which is important for the accurate description of the electronic structure of atoms and molecules. The conventional

application of MBPT involves an order by order perturbation expansion. Truncations at second order are the most popular. However, there are many problems of interest where the second order calculations are not sufficient and where higher order calculations are often required.

The straightforward order by order expansion is now possible up to fourth order.²⁻⁹ Fourth order MBPT calculations are quite accurate for most applications, but require considerable amounts of computation due to the large number of triple excitations necessary for the full calculations. One way of incorporating some contributions from higher level excitations into the lower order calculations is the use of several reference configurations and lower orders as is done in many configuration interaction type methods. The MBPT approach, based upon several reference states, is called a multi-reference many-body perturbation theory (MRMBPT) and can be formulated to have a significant computational advantage over the higher order single reference state methods.¹⁰⁻¹³ In addition, some systems, such as those with multiple bonds, require multi-reference states even for qualitative descriptions.

The MRMBPT method developed by Freed and coworkers¹²⁻¹⁸ is one of the most widely applied methods among the various MRMBPT methods developed recently. The MRMBPT method of Freed *et al.* is based upon a quasidegenerate many-body perturbation theory of the Rayleigh-Schrödinger type and is usually called an effective valence shell Hamiltonian method. The method can also be viewed as a perturbation-variation method since the final energies are obtained through the diagonalization of an effective Hamiltonian in the valence space. The present method has been successfully applied in the study of electron correlation in atoms and molecules, including transition method atoms.¹³⁻¹⁸

These second order MRMBPT calculations have been gauged by comparisons with experimental data, a procedure which can be misleading for a number of reasons. The results of second order calculations contain corrections due to the use of incomplete basis sets, the omission of higher order terms and the neglect of relativistic corrections. Even the third order calculations, which have been performed only for a limited number of cases, suffer from similar deficiencies when the experimental values are taken as standards. On the other hand, the comparison of MRMBPT calculations with the corresponding configuration interaction calculations (CI) yields a more concrete test of the multi-reference methods.

In this work, the MRMBPT method of Freed *et al.*¹²⁻¹⁸ is tested for several four-valence-electron states of the transition method atom and ions Ti, V⁺ and Cr²⁺ by comparing MRMBPT calculations with the corresponding CI calculations.¹⁹ CI calculations on these systems are complicated by the large number of configurations that should be included in the calculation, especially in view of the "softness" of the 3s and 3p portions of the core orbitals.^{15,20,21} Therefore, both calculations are performed in truncated orbital spaces with frozen core approximations. Direct comparison between the second order MRMBPT calculations and the CI calculations enables a check of approximations invoked by these two methods.

The MRMBPT calculations can be performed including core-core and core-valence correlation, whereas this becomes exceedingly difficult with CI methods and larger basis sets because of the need for too many configurations and because

there are too many electrons then being correlated to have the calculations be size consistent. Hence, the explicitly size consistent MRMBPT calculations can provide an estimate of the core-core and core-valence contributions neglected in the CI approaches. On the other hand, given the frozen core approximation the CI calculations provide an estimate of the error in the second order MRMBPT computations due to the neglect of higher orders of perturbation theory. The central importance of transition metal systems and the technical complexity associated with accurate *ab initio* calculations for them both make it very useful to utilize different theoretical models to assess the important physical effects.

Satisfactory agreement is found between the two methods in the frozen core approximation despite the following differences in the methods. The perturbation theory is size-extensive, while a truncated CI calculation is not. The perturbation solutions depend on the choice of the zeroth order state, while the CI has a unique solution. In the following sections, a brief description of the method and the computations is given and the results are discussed.

Methods and Calculations

The present MRMBPT method can be considered as an approximate reduction of the full space Schrödinger equation into that for a smaller reference state. The detailed description of the formalism is available in the literature,^{13,22} and only a brief sketch is summarized here.

The basic concept of the underlying principles is most simply illustrated by the partitioning technique.²⁴ The Schrödinger equation of the system is

$$H\phi = E\phi \quad (1)$$

where H refers to the nonrelativistic Hamiltonian, ϕ to the wavefunction and E is the energy of the system. Although the exact solution of eq.(1) is not obtainable for many electron systems, the determinantal space (or configuration space) required for the full description of the wavefunction ϕ can be formally partitioned into two parts, the reference space P and its orthogonal complement Q,

$$P = \sum |v\rangle \langle v| \quad (2)$$

$$Q = 1 - P = \sum |e\rangle \langle e| \quad (3)$$

where $|v\rangle$ refers to a reference determinant, and $|e\rangle$ is a determinant not belong to the reference space. Then, the effective Hamiltonian for the reference space, H^{eff} , may be formally written as

$$H^{eff} = PHP + PHQ(E - QHQ)^{-1}QHP, \quad (4)$$

where H is now a matrix representation of the Hamiltonian.

The second term of eq.(4) contains the inverse of an infinite dimensional matrix, due to the infinite number of configurations in Q space, and has to be approximated. The present method employs Rayleigh-Schrödinger type perturbation theory using a complete reference space and a finite number of orbitals and basis functions. The theoretical as well as the computational framework for the present MRMBPT is developed by Freed and coworkers as mentioned earlier. The approach is also known as the effective valence shell

Hamiltonian method because the reference space P is usually selected as a complete space including all configurations generated by all valence orbitals and valence electrons.

The present method is implemented up to third order; the highest order for which the effective Hamiltonian has been obtained.^{13,25} The first order calculation is an ordinary CI within the reference space, the matrix defined by P in Figure 1. Higher order calculations use perturbation theory to add contributions from the excited space Q to modify the matrix elements within the reference space P . Then the energies for each order are obtained by diagonalizing the corresponding modified matrix (the effective Hamiltonian matrix $H^{(n)}$). Through third order, the contributing configurations in the Q space are only those that correspond to single or double excitations with respect to P space. The off-diagonal elements in Q space do not contribute in second order, but are taken into account in the third order calculations as explained in Figure 1. When the orbital space is small, a CI calculation can be performed for the whole space and contains all the configurations contributing to the second order calculations. The comparison of second order MRMBPT calculations with the corresponding CI calculations, using exactly the same orbitals and configuration space, provides useful information on the accuracy of both methods as explained in the introduction.

In this work, the transition metal atoms and ions Ti, V*, and Cr** are selected for the comparison because extensive studies are available for the species from a previous work.¹⁵ Core, valence and excited orbitals are generated from SCF calculations for the $^3F(d^2s^2)$ state of Ti, the $^5F(d^3s^1)$ state of V* and the $^5F(d^3s^1)$ state Cr** with 8s6p3dlf basis sets of Slater type functions (STF) described earlier.¹⁵ In order to reduce the number of configurations in CI calculations to a reasonable size, correlation energies are computed with the frozen core

	P	Q
P	0 1 1 . .	2 2 2 2 . . .
	1 0 1 . .	2 2 2 2 . . .
	1 1 0 . .	2 2 2 2 . . .

Q	2 2 2 . .	2 3 3 3 . . .
	2 2 2 . .	3 2 3 3 . . .
	2 2 2 . .	3 3 2 3 . . .
	2 2 2 . .	3 3 3 2 . . .

Figure 1. Partitioning of the Hamiltonian matrix for MRMBPT calculations. The matrix elements denoted by 0, 1, 2, and 3 begin to contribute from the zeroth, the first, the second and the third order MRMBPT calculations, respectively. The dimension of the matrix to be diagonalized in all orders is the same as the number of configurations (or determinants) in P space. Through third order the configurations in Q space are restricted to single and double excitations relative to configurations in P space.

(FC) approximation where the 1s, 2s, 2p, 3s, and 3p orbitals are considered as core orbitals and 3d and 4s as valence orbitals. In the second order MRMBPT calculations, the reference space P of Figure 1 contains all the distinct atomic configurations with four electrons distributed in the 4s and 3d orbitals. The excited space Q of Figure 1 contains configurations with three or two electrons in the valence orbitals and one or two electrons, respectively, in the excited orbitals. Excited orbitals for the present case are orbitals which have higher orbital energies than the 4s and 3d orbitals and thus are not occupied in the SCF calculations. The CI calculations have been performed using the same orbitals and configurations¹⁹ as for the MRMBPT work. For computational reasons, the CI calculations are available only for a limited number of valence states. Some of the CI calculations are further simplified by excluding a few energetically unimportant orbitals from the excited orbital space, and the corresponding MRMBPT calculations were also performed using the same truncated orbital space.

Results and Discussion

Selected excitation energies for Ti, V* and Cr** are summarized in Tables 1 through 6. Experimental values²⁶ and the full space second order MRMBPT values from a previous work¹⁵ are also shown for comparison. It is noted that the

Table 1. Selected Excitation Energies (in eV) of Ti Calculated with Orbitals Generated from SCF Calculations of the 3F State Using a 8s6p3dlf STF Basis Set

State ^a	CI ^c	Frozen Core ^b full space		EXP ^e
		MRMBPT	MRMBPT ^d	
$^3F(d^2s^2)$	0.0	0.0	0.0	0.0
$^1G(d^2s^2)$	0.56	0.61	0.86	0.67
$^3P(d^2s^2)$	1.12	1.19	0.96	0.70
$^3G(d^2s^2)$	1.30	1.41	1.30	1.04
$^3H(d^2s^2)$	1.77	1.89	1.85	1.41
$^1P(d^2s^2)$	1.85	2.12	1.93	1.65
$^1G(d^2s^2)$	2.08	2.28	2.27	1.74
$^3D(d^2)$	4.33	4.51	2.61	2.74
$^1F(d^2s^2)$	3.08	3.29	2.96	2.86

^adominant configurations in parentheses. ^bno excitations allowed from the core orbitals 1s, 2s, 2p, 3s and 3p. ^cfrom Ref. 19. ^dfrom Ref. 15. ^efrom Ref. 26.

Table 2. Selected Excitation Energies (in eV) of Ti Calculated with Orbitals Generated from SCF Calculations of the 3F State Using a 8s6p3dlf STF Basis Set

State ^a	CI ^c	FC-(7s,8s,7p) ^b full space		EXP ^e
		MRMBPT	MRMBPT ^d	
$^3F(d^2s^2)$	0.0	0.0	0.0	0.0
$^1D(d^2s^2)$	1.03	1.09	0.91	0.87
$^3P(d^2s^2)$	1.22	1.25	1.01	1.03
$^3D(d^2s^2)$	2.83	3.06	2.32	2.14

^adominant configurations in parentheses. ^bin addition to the frozen core approximations of Table 1, the excited orbitals 7s, 8s and 7p are also omitted. ^cfrom Ref. 19. ^dfrom Ref. 15. ^efrom Ref. 26.

reference states in the tables are not necessarily the actual ground states of the atoms or ions.

The excitation energies of Ti calculated with the second order MRMBPT method agree well with those from the CI calculations as shown in Table 1. The largest discrepancy is 0.27 eV for $^1P(3d^34d^2)$ state. The difference between the MRMBPT and CI excitation energies tends to increase with increasing excitation energy. The same trend is found for the excitation energies calculated with the truncated excited space as shown in Table 2. In this particular scheme of truncation, where excited orbitals 7s, 7p and 8s are omitted, the truncation error is expected to be very small since the orbitals are largely the orthogonal partners of the core orbitals neglected in the calculation of correlation contributions.

Inclusion of core relaxation in the MRMBPT calculations improves the agreement with experiment for most excitation energies as can be seen from the numbers in the columns marked as "full space MRMBPT" in Tables 1 and 2. If the contributions from excitations from core orbitals is similar for CI and MRMBPT calculations, we expect very good agreement between experimental excitation energies and CI excitation energies which would be computed including core correlation energies. Conversely, if the third order contributions are mainly responsible for the difference between frozen core CI and MRMBPT calculations, these third order

Table 3. Selected Excitation Energies (in eV) of V^+ Calculated with Orbitals Generated from SCF Calculations of the 3F State Using a 8s6p3d1f STF Basis Set

State ^a	CI ^c	Frozen Core ^b full space		
		MRMBPT	MRMBPT ^d	EXP ^e
$^3D(d^4)$	0.0	0.0	0.0	0.0
$^3F(d^3s^1)$	0.01	0.01	0.43	0.34
$^3H(d^4)$	1.88	1.88	1.88	1.54
$^3P(d^3s^1)$	1.68	1.60	1.75	1.67
$^3G(d^4)$	1.91	1.82	2.29	2.01
$^1G(d^4)$	2.35	2.25	2.40	2.20
$^1P(d^3s^1)$	2.78	2.73	2.96	2.74
$^1H(d^3s^1)$	3.00	2.91	3.31	2.87
$^1F(d^4)$	3.88	3.81	3.58	3.30

^adominant configurations in parentheses. ^bno excitations allowed from the core orbitals 1s, 2s, 2p, 3s and 3p. ^cfrom Ref. 19. ^dfrom Ref. 15. ^efrom Ref. 26.

Table 4. Selected Excitation Energies (in eV) of V^+ Calculated with Orbitals Generated from SCF Calculations of the 3F State Using a 8s6p3d1f STF Basis Set

State ^a	FC-4f ^b		FC-(7s,8s,7p) ^c full space			
	CI ^c	MRMBPT	CI ^c	MRMBPT	MRMBPT ^d	EXP ^e
$^3F(d^3s^1)$	0.0	0.0	0.0	0.0		
$^3P(d^4)$	0.81	0.86	0.67	0.73	0.25	0.35
$^3D(d^4)$	1.62	1.65	1.51	1.56	1.12	1.17
$^1D(d^4)$	1.90	1.92	1.80	1.82	1.49	1.49

^adominant configurations in parentheses. ^bin addition to the frozen core approximations of Table III, the 4f excited orbitals are also deleted. ^cfrom Ref. 19. ^dsimilar to b, but the deleted excited orbitals are 7s, 8s and 7p. ^efrom Ref. 15. ^ffrom Ref. 26.

MRMBPT calculations without the frozen core approximations would yield excitation energies considerably closer to the experimental values than the second order calculations.

The second order MRMBPT and CI calculations agree to within 0.1 eV for all states of V^+ shown in Table 3 and 4, indicating that very little change is expected from the higher order contributions. Agreement with experiment is slightly better without contributions from core excitations when the excitation energies are measured relative to the $^3D(d^4)$ state as shown in Table 5. On the other hand, the opposite is true when they are measured relative to the $^3F(d^3s^1)$ state as described in Table 4. It appears that the $^3D(d^4)$ state is excessively lowered in energy by core excitation contributions, by about 0.2 eV for this MRMBPT calculation. In contrast, the $^3F(d^3s^1)$ state becomes too low by 0.3-0.4 eV relative to other states if core excitations are neglected. Without core excitations, the contributions from f orbitals alter excitation energies by less than 0.1 eV. This is interesting because the f functions contribute significantly when core excitations are included.^{15,20,21,22}

Discrepancies of 0.2-0.3 eV between second order MRMBPT and CI calculations are observed for interconfigurational excitations of Cr^{2+} in Table 5. The differences are much smaller for excitations between states within the same configurations in Table 5 and 6, but they increase slightly with the excitation energy. The effect of core excitations on Cr^{2+} excitations is about 0.3 eV and does not display any obvious

Table 5. Selected Excitation Energies (in eV) of Cr^{2+} Calculated with Orbitals Generated from SCF Calculations of the 3F State Using a 8s6p3d1f STF Basis Set

State ^a	CI ^c	Frozen Core ^b full space		
		MRMBPT	MRMBPT ^d	EXP ^e
$^3D(d^4)$	0.0	0.0	0.0	0.0
$^3H(d^4)$	2.34	2.39	2.12	2.12
$^3G(d^4)$	2.85	2.94	2.35	2.25
$^1F(d^4)$	5.12	5.23	4.74	5.05
$^3F(d^3s^1)$	6.15	5.87	6.17	6.16
$^1G(d^4)$	3.50	3.59	3.17	—
$^3P(d^3s^1)$	8.07	7.85	7.81	7.80
$^1H(d^3s^1)$	9.57	9.36	9.69	8.81

^adominant configurations in parentheses. ^bno excitations allowed from the core orbitals 1s, 2s, 2p, 3s and 3p. ^cfrom Ref. 19. ^dfrom Ref. 15. ^efrom Ref. 26.

Table 6. Selected Excitation Energies (in eV) of Cr^{2+} Calculated with Orbitals Generated from SCF Calculations of the 3F State Using a 8s6p3d1f STF Basis Set

State ^a	FC-4f ^b		FC-(7s,8s,7p) ^c full space			
	CI ^c	MRMBPT	CI ^c	MRMBPT	MRMBPT ^d	EXP ^e
$^3P(d^4)$	0.0	0.0	0.0	0.0	0.0	0.0
$^3F(d^4)$	0.11	0.12	0.16	0.18	0.25	0.12
$^3D(d^4)$	1.27	1.28	1.29	1.31	1.10	0.12

^adominant configurations in parentheses. ^bin addition to the frozen core approximations of Table III, the 4f ^cfrom Ref. 19. ^dsimilar to b, but the deleted excited orbitals are 7s, 8s and 7p. ^efrom Ref. 15. ^ffrom Ref. 26.

trend for the second order MRMBPT calculations. If the effects of core excitations are transferred from MRMBPT to CI calculations, no significant improvement in the agreement with experiment is anticipated by including core excitations in calculating CI excitation energies of Cr⁺.

Among the species studied in this work, the excitation energies of V^{*} display remarkable agreement between the MRMBPT and CI calculations, indicating that the higher order contribution in MRMBPT calculations can be made unimportant by a judicious choice of valence orbitals. Even second order MRMBPT calculations for Ti and Cr⁺ are reasonably converged, a feature reinforced by the smallness of previously computed third order contributions.¹⁵ The present comparison between second order MRMBPT and CI calculations reconfirms the reliability of the former in studying the important correlation effects involved in the proper description of the electronic structure of transition metal atoms. Earlier studies also indicate that the second order MRMBPT calculations are useful for many other systems¹³⁻¹⁸ method. Although the present knowledge of the method is by no means exhaustive, an efficient version of the present MRMBPT method marks an excellent addition to general purpose *ab initio* packages. Extensive studies of potential surfaces of polyatomic systems with this method will become practical and very interesting.

Acknowledgement. The research at KAIST is, in part, supported by Korean Science and Engineering Foundation, while that at chrego is supported, in part, by NSF CHE 83-17098. The support of Wrubel Computer Center at Indiana University is gratefully acknowledged.

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