Theor Chim Acta (1995) 90: 273–290

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Chimica Acta

The multiconfigurational spin tensor electron propagator method (MCSTEP): Comparison with extended Koopmans' theorem results

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Received March 29, 1994/Final revision received May 10, 1994/Accepted August 24, 1994

Summary. We applied the multiconfigurational spin tensor electron propagator method (MCSTEP) for determining the lowest few (in energy) vertical ionization potentials (IPs) of HF, H_2O, NH_3, CH_4, N_2, CO, HNC, HCN, C_2H_2, H_2CO, and B_2H_6. We chose these molecules so that we could compare MCSTEP IPs with recently reported extended Koopmans' theorem (EKT) IPs on the same molecules. Using standard Dunning core-valence basis sets with relatively small complete active spaces, MCSTEP results are in very good to excellent agreement with experiment. These MCSTEP IPs are obtained using matrices no larger than 400 × 400. EKT matrices are even smaller; however, to obtain similar but generally slightly worse agreement with experiment, fairly large active spaces are required with EKT.

Key words: Ionization – Propagators – Ionization potential – MCSTEP – Green's functions

1. Introduction

With single particle Green's function (or electron propagator) methods vertical ionization potentials (IPs) and electron affinities (EAs) are obtained directly rather than by separately determining the total electronic energies of the neutral and ions and subtracting to obtain energy differences [1, 2]. Electron propagator IPs and EAs are exact in principle; however, in practice, approximations are made in order to obtain solutions.

Green's function/electron propagator vertical IPs and EAs are traditionally obtained approximately via a perturbative approach to solving the equations [1–12]. In order to obtain IPs and EAs the equations are usually solved consistently through at least third order. Often some estimate of higher-order corrections is also made. Third and higher-order perturbative solutions for the single particle Green's function/electron propagator are accurate most of the time when the initial (or reference) state is closed shell and also is predominately a single configuration (i.e. nondynamical correlation is unimportant). For these kinds of systems, outer valence, principal, vertical IPs can typically be calculated to ± 0.3 eV or sometimes better. Occasionally, there are also serious problems using perturbative approaches to obtain reliable IPs and EAs even when they are *a priori* expected to work well [13, 14].

The multiconfigurational spin tensor electron propagator method (MCSTEP) [15] is an alternative procedure for obtaining approximate solutions to the single particle Green's function/electron propagator. It is based on an explicitly multiconfigurational initial state and explicitly employs angular momentum coupling methods for spin. Electron ionization and attachment energies are directly obtained between initial and final states of pure spin symmetry even when these states have large non-dynamical correlation and/or are open shell.

The predecessor of MCSTEP is known as the multiconfigurational electron propagator method (MCEP) [16]. Both methods can be applied to open shell as well as highly correlated systems. They give essentially identical results [17]. The difference between the two methods is that MCEP directly uses the spin ladder operators, S_+ and S_-, while MCSTEP uses the methods of angular momentum coupling explicitly. Therefore, MCEP is rather cumbersome theoretically.

MCSTEP and MCEP can be derived straightforwardly from single particle Green's function and electron propagator theory [15, 16]. The principle differences between more usual perturbative approaches and MCSTEP/MCEP are in the choices of initial state and the operator manifold. Hence, the powerful techniques and information of Green's function/propagator methodology are directly applicable to MCSTEP and MCEP. However, the (sometimes severe) limitations of the perturbative approaches – most importantly, the possibility of non-convergent or slowly convergent expansions [13, 14] – are not present with MCSTEP and MCEP since perturbation theory is not used.

In this paper we apply the MCSTEP procedure for calculating the lower ionization potentials of HF, H_2O, NH_3, CH_4, N_2, CO, HNC, HCN, C_2H_2, H_2CO, and B_2H_6. These systems have been studied experimentally as well as theoretically [18–31]. We specifically choose these molecules since Morrison and Liu [29] have recently reported calculations for their lower-lying IPs using the extended Koopmans' theorem (EKT) method. Hence, the MCSTEP calculations reported here allow comparison and contrast with the EKT calculations.

These molecules all have closed shell initial states. The power of MCSTEP is, of course, most evident when the initial state is open shell and also when non-dynamical correlation effects are important. We have several times previously successfully applied both MCEP and MCSTEP for open shell [16, 17, 32–36] as well as for closed shell systems [14–16, 34, 36–38]. Both MCSTEP and EKT are designed to accurately determine IPs when initial state non-dynamical correlation is present. To our knowledge, EKT, however, has not as yet been formulated or developed for systems with open shell initial states. Even though the molecules here have closed shell initial states and may not have important non-dynamical correlation, this is the first work where explicit comparisons between MCSTEP and EKT have been done for a series of molecules.

In a recent paper [34] we compared the MCSTEP IPs of CH_2 to the Δ full CI values using the exact same basis set and at the same geometries. Δ full CI results are, of course, the exact result for a given choice of basis set. For lowest three IPs MCSTEP values differed by 0.05, 0.11, and 0.05 eV from Δ full CI IPs. For all the IPs in CH_2 below 19.0 eV MCSTEP results were no more than 0.22 eV different than the Δ full CI IPs. These MCSTEP calculations included some IPs both from the $X\,^3B_1$ ground state and from the first excited $^1A_1$ state as the initial (reference) state to open shell ionic states.

We have also previously compared MCEP and MCSTEP with the more usual perturbative formulations of electron propagator theory [14, 16, 37, 38]. In those works we showed that MCEP and MCSTEP are as reliable as third and higher-order electron propagator methods when the latter work well [14, 16, 37].

Unfortunately, there are several cases where the perturbative approaches to electron propagator methods break down and are unreliable [13, 14, 38] even when the initial state is closed shell and non-dynamical correlation effects are expected to be relatively unimportant [13, 14]. For these systems it was *a priori* expected that third and partial fourth order electron propagator methods would work well [13]. Third and partial fourth-order calculations by Ortiz [13] convincingly demonstrated that these perturbative electron propagator procedures would sometimes not give accurate results. Using exactly the same basis sets and geometries as in Ref. [13], MCSTEP gave reliable, accurate values in these cases where third order and partial fourth-order electron propagator methods were unreliable [14].

Hence, since in this paper the purpose is to compare MCSTEP with the EKT method and since we have already several times compared MCSTEP with various perturbative approaches to the electron propagator [14, 16, 37, 38], we will not present further comparisons with third and higher-order electron propagator approaches. Such further comparisons are completely unnecessary and redundant and would provide no additional information than is already available elsewhere [14, 16, 37, 38].

In Section 2 we briefly describe the MCSTEP and EKT methods. In Section 3 we present and discuss our results. Finally, we conclude and summarize.

2. Theory

In this section some of the theory relevant to MCSTEP and EKT is very briefly discussed. We do not intend this section to be complete, but instead to be indicative of the methodology. For a more complete discussion, we direct interested readers to the original papers on MCEP [16], MCSTEP [15], and EKT [39–41]. For a summary on MCEP and MCSTEP longer than given here, interested readers should examine Ref. [36].

2.1. MCEP and MCSTEP

The original formulations of MCEP and MCSTEP were in terms of Green's function/electron propagator theory [15, 16]. Hence, the powerful techniques of those theories are directly applicable to MCSTEP.

The poles of the single particle Green's function are the ionization potentials and electron affinities of a system. In general, these poles cannot be obtained exactly. Therefore, approximations have to be made. There are two principal approximations: for the exact initial state (also known as the reference state) and for the complete operator manifold that describes the ionization or attachment processes [1–17].

The Green's function/electron propagator equations were traditionally solved for closed shell atoms and molecules by approximating the reference state by a single determinant Hartree–Fock state corrected by Møller–Plesset perturbation theory [1–13]. In these techniques operators were included in the operator manifold to assure the solution of the resulting equations correctly through a certain order in the electron–electron interaction. To obtain fairly accurate and reliable ionization potentials for outer valence principal IPs for closed shell systems that had initial states well described in zero order by a single determinant Hartree–Fock wavefunction, it was found that for ionization potentials the equations needed to be solved at least through third order in the electron–electron interaction. Some higher-order terms are sometimes required in the approximate Green's function solution in order to obtain accurate IPs.

Although these third and third + order perturbative Green's function/electron propagator methods have sometimes been very successful [1–12], they are also limited in applicability. Perturbative approaches usually cannot handle reliably or at all systems with initial states that are open shell and/or highly correlated (non-dynamical correlation) [38] for either IPs or EAs. Sometimes perturbative approaches to Green's function/electron propagator methods do not work very well at all even when the initial state is closed shell and initial state correlation effects are relatively small [13, 14].

With MCSTEP these problems are solved by using a multiconfigurational reference state and explicitly coupling tensor ionization and attachment operators to a tensor initial state. For calculational simplicity an MCSCF reference state is usually used in MCSTEP, although a CI state or other nonperturbatively correlated state could also be used. The operator manifold chosen for MCSTEP includes simple electron addition and destruction operators, $N-1$ transfer operators which remove an electron from the occupied/partially occupied orbitals and allow all possible rearrangements of the remaining electrons in the partially occupied space, and $N+1$ transfer operators which add an electron to the unoccupied/partially unoccupied orbitals and allow all possible rearrangements of the remaining electrons in the partially occupied space [15, 16].

MCSTEP IPs and EAs are obtained from the generalized eigenvalue equation

$$MX_{\mathrm{f}} = \omega_{\mathrm{f}} N X_{\mathrm{f}}, \tag{1}$$

where

$$\begin{aligned} M_{\mathrm{r,p}} = \sum_{\Gamma} (-1)^{S_0 - \Gamma - S_{\mathrm{f}} - \gamma_{\mathrm{r}}} W(\gamma_{\mathrm{r}}\gamma_{\mathrm{p}} S_0 S_0; \Gamma S_{\mathrm{f}})(2\Gamma + 1)^{1/2} \\ \times \langle\langle N S_0 \| \{h_{\mathrm{r}}^{+}(\bar{\gamma}_{\mathrm{r}}), H, h_{\mathrm{p}}(\gamma_{\mathrm{p}})\}^{\Gamma} \| N S_0 \rangle\rangle \end{aligned} \tag{2}$$

and

$$\begin{aligned} N_{\mathrm{r,p}} = \sum_{\Gamma} (-1)^{S_0 - \Gamma - S_{\mathrm{f}} - \gamma_{\mathrm{r}}} W(\gamma_{\mathrm{r}}\gamma_{\mathrm{p}} S_0 S_0; \Gamma S_{\mathrm{f}})(2\Gamma + 1)^{1/2} \\ \times \langle\langle N S_0 \| \{h_{\mathrm{r}}^{+}(\bar{\gamma}_{\mathrm{r}}), h_{\mathrm{p}}(\gamma_{\mathrm{p}})\}^{\Gamma} \| N S_0 \rangle\rangle, \end{aligned} \tag{3}$$

ω_{f} is an IP or EA to the final ion tensor state $|N \pm 1\, S_{\mathrm{f}}\rangle\rangle$ which has spin S_{f}. W is the usual Racah coefficient, $h_{\mathrm{p}}(\gamma_{\mathrm{p}})$ and $h^{+}{}_{\mathrm{r}}(\bar{\gamma}_{\mathrm{r}})$ are tensor operator versions of members of the operator manifold with ranks γ_{p} and γ_{r}, respectively. $\{\,,\}$ is the anticommutator

$$\{A,B\} = AB + BA, \tag{4}$$

and $\{\,,,\}$ is the symmetric double anticommutator

$$\{A,B,C\} = \tfrac{1}{2}\{A,[B,C]\} + \tfrac{1}{2}\{[A,B],C\}. \tag{5}$$

The resulting MCSTEP matrices are usually no more than 400 × 400 with strict dimension limitations imposed by an approximate energy criteria to limit the number of operators included [15, 16].

For the IPs for the molecules reported in this paper, all initial states are closed shell so the tensor coupling machinery present in MCSTEP is not necessary or used. Several previous MCEP and MCSTEP calculations where the initial state was open shell have previously been reported [16, 17, 32–36].

We have previously demonstrated that MCSTEP is very accurate and reliable for lower-lying (in energy) IPs [14–17, 32–38]. These are the IPs corresponding to processes that are primarily simple electron removal (i.e. the principal IPs) of the outer valence electrons. MCSTEP shake-up IPs (where the primary processes correspond to simple electron removal with excitation of the remaining electrons) are generally only of qualitative accuracy [14, 15, 34, 35, 37, 38].

MCSTEP IPs are not as accurate when important contributions from processes that are simple electron removal + excitation of the remaining electrons to diffuse orbitals are necessary for an accurate description [14, 15, 34, 35, 37, 38]. This is true regardless of the number of diffuse functions in the basis set since the transfer type operators included in MCSTEP allow only for excitation of electrons in orbitals in the valence space and not to virtual orbitals which may be diffuse. These IPs are usually higher in energy and may include most of the inner valence and core principal IPs as well as most of the shake-up IPs.

We have previously shown that these higher-lying shake-up IPs and higher-lying principal IPs can be accurately determined by an extension of MCSTEP known as the repartitioned multiconfigurational spin-tensor electron propagator method (RMCSTEP) [15]. RMCSTEP is more complicated than MCSTEP and is unnecessary to use for the comparisons here with IPs obtained via EKT since the later technique allows only for the determination of low-lying principal IPs (see below).

2.2. *EKT*

With EKT the ionization potentials are obtained by solving the generalized eigenvalue equation [39–41]

$$V\underset{\sim}{c} = \varepsilon_f \gamma \underset{\sim}{c}, \tag{6}$$

where

$$V_{ij} = -\langle 0 | a_i^{+} [H, a_j] | 0 \rangle \tag{7}$$

and

$$\gamma_{ij} = \langle 0 | a_i^{+} a_j | 0 \rangle . \tag{8}$$

$|0\rangle$ is an MCSCF or CI initial state, a_i^{+} is an electron creation operator, and a_j is an electron destruction operator, and ε_f is the ionization potential to the final state $|f\rangle$.

Thus, with the EKT method only simple electron destruction operators from doubly or partially occupied orbitals are included while with MCSTEP simple destruction/creation operators for electrons in all orbitals are included; IP and EA transfer operators that are included in MCSTEP are not present in EKT; the matrix elements in EKT are somewhat different than for MCSTEP; there is no coupling between IPs and EAs in EKT as there is in MCSTEP; and since there is no explicit tensor coupling, EKT IPs starting from open shell initial states will not in general be to states of pure symmetry.

Because the operator manifold in EKT includes only simple electron removal operators from the doubly and partially occupied orbitals, it is only the lower lying (in energy) principal IPs that can be accurately described with EKT. The EKT matrices are small (and smaller than the MCSTEP matrices) since they are the dimension of the number of doubly and partially occupied orbitals of a certain symmetry.

Because none of the transfer operators that are present in MCSTEP are included in the EKT method, it is expected that a much larger number of initial state configurations will be necessary for the same accuracy as obtained by MCSTEP IPs. However, the calculation of matrix elements involving transfer operators is also the most computationally time consuming step in MCSTEP. (Although neither the EKT or MCSTEP methods are computationally very time consuming.)

3. Results and discussion

In the calculations reported here we used basis sets obtained from the pVTZ and pVDZ correlation consistent basis sets of Dunning (Ref. [42]). The pVDZ basis set was chosen for B_2H_6 while pVTZ was chosen for the other molecules. For a few molecules we also tried to duplicate the basis sets used in the EKT calculations in Ref. [29]; however, we were unable to do that exactly for any system. All six Cartesian d function components and all 10 Cartesian f functions components were included in the basis sets in all our calculations. The geometries used in all our calculations were the same as those used in Ref. [29].

We usually use a CAS MCSCF wavefunction as the MCSTEP initial state. With this choice as the MCSTEP initial state, we have previously shown that for lower lying vertical IPs MCSTEP calculations are accurate and reliable [14–17, 32–38]. An extensive discussion about the CAS choices for MCSTEP can be found in Refs. [14, 15].

All the MCSCF stationary points that we obtained fulfilled criteria that we previously called "proper" and "desired" [43]. However, a few of these stationary points we obtained had another unwanted characteristic; namely, that the eigenvalues of the Lagrangian (approximate "orbital energies") were in an unexpected order. That is, occasionally one of the Lagrangian eigenvalues for the doubly occupied orbitals would be higher than some of the eigenvalues for the orbitals is the partially occupied space.

Sometimes we were able to get the wanted, unscrambled order by making a different initial guess for the MCSCF orbitals. In a few cases for the CASs we used we were unable to obtain this order no matter what we did. There is, of course, no guarantee that a proper stationary point exists on the CAS space energy hypersurface that has all the properties we desire and want.

One possible solution to this scrambling problem is to use larger CASs. For example, an all valence CAS choice would very often not, in general, have this problem. A difficulty with this approach, however, is that all valence CASs have prohibitively large number of configurations for large systems. We are also somewhat restricted computationally since our MCSTEP programs are first generation code and are not designed for use with many configurations. Finally, and most importantly, by keeping the number of configurations fairly small we can demonstrate that large active spaces are probably not necessary in order to obtain accurate low-lying principal IPs.

In order to solve this occasional problem of the scrambling of the approximate orbital energies between the doubly occupied and partially occupied orbital spaces, we would restrict the MCSCF optimization by excluding one $i \leftrightarrow j$ (doubly occupied $\leftrightarrow$ partially occupied) orbital rotation. Doing this is usually enough to give the wanted order of the Lagrangian eigenvalues. The reference state obtained in this fashion is, of course, not the true, wanted MCSCF state but rather is a good approximation to it. (Note that upon converging to these approximate MCSCF states convergence to the wanted MCSCF state usually cannot be obtained by subsequently placing the $i \leftrightarrow j$ rotation back in. Instead the fully optimized MCSCF state subsequently obtained usually again would have the scrambled order for the Lagrangian eigenvalues.) As mentioned above, an MCSCF state is, strictly speaking, not required in MCSTEP. We have found that this approximation to the MCSCF stationary point works fine for the initial MCSTEP state.

Unless we indicate otherwise in the following, fully optimized CAS MCSCF states for the ground state of the neutral molecule were used as the initial (reference) states for MCSTEP. When the eigenvalues of the converged MCSCF Lagrangian were in a scrambled order and it was impossible to obtain an MCSCF state with the correct ordering, an approximate MCSCF state was used where one rotation was excluded in the optimization. Upon convergence of this (approximate) MCSCF state, the eigenvalues of its Lagrangian were checked to assure they were in the wanted order.

In our calculations reported below we only used in MCSTEP initial states with the wanted structure of the Lagrangian eigenvalues. In test calculations where the initial state had an unwanted ordering of the Lagrangian eigenvalues, MCSTEP IPs often differed farther from experiment than when an MCSTEP initial state was used which had the correct ordering of the Lagrangian eigenvalues.

For each molecule below, we compare our results both with experimental values and the best EKT calculations reported in Ref. [29].

3.1. *HF*

With the pVTZ basis set the SCF energy is -100.0584 a.u.

The CAS we used is ($3\sigma 1\pi 4\sigma 2\pi$). This CAS has 112 determinants for the ground state. The converged MCSCF energy is -100.1556 a.u. The approximate orbital energies (eigenvalues of the Lagrangian) are in the correct order; hence, this MCSCF wavefunction was used as the initial state in subsequent MCSTEP calculations.

In Table I we list the two lowest MCSTEP vertical ionization potentials for HF and compare these results with experiment [21]. Our results are in excellent agreement with experiment, differing from experiment by -0.15 eV for the 1π IP and 0.07 eV for the 3σ IP.

For this molecule we also tried to perform MCSTEP calculations with the basis set used in Ref. [29]. The $\langle 5s3p1d/3s1p \rangle$ Dunning [44] basis set obtained in the MESSKIT suite of codes [45] gave an SCF energy of -99.9274 a.u. while the $\langle 5s3p1d/3s1p \rangle$ basis reported in Ref. [29] as from Dunning and Hay [46] gave -100.0601 a.u. (However, note that no $\langle 5s4p1d \rangle$ F or $\langle 3s1p \rangle$ H basis sets are listed in Ref. [46].)

Using the same CAS as we used with the pVTZ basis the MCSCF energy with our $\langle 5s3p1d/3s1p \rangle$ basis is -100.0205 a.u. The eigenvalues of the Lagrangian for this basis set were in the wanted order so this wavefunction was used as the initial state in subsequent MCSTEP calculations.

The MCSTEP and best previously reported EKT results [29] with these bases are also given in Table 1. The best reported EKT (calculation II) ground state wavefunction in Ref. [29] contained 5180 terms in C_{2v} symmetry. The 1π MCSTEP IP is 16.06 eV, the EKT IP is 16.27 eV, and experiment [19] is 16.19 eV. The 3σ MCSTEP IP is 20.10 eV, the EKT IP is 20.35 eV, and experiment [21] is 19.9 eV.

As a test we also used a pVTZ approximate MCSCF stationary point where the $2\sigma \leftrightarrow 3\sigma$ rotation was not included as the initial state in MCSTEP. As noted above, the eigenvalues of the Lagrangian for the fully optimized MCSCF with this CAS and the basis set are in the wanted order. Hence, this will provide a control for other calculations where the order of the eigenvalues of the Lagrangian for a fully optimized MCSCF stationary point is incorrect. The eigenvalues of the Lagrangian of this approximate MCSCF state are in the wanted order so this wavefunction was used in the subsequent MCSTEP calculation.

The 1π MCSTEP IP with the approximate MCSCF initial state is 0.07 eV larger than the MCSTEP IP with the fully optimized pVTZ MCSCF initial state. The 3σ MCSTEP IP with the approximate pVTZ MCSCF initial state is only 0.02 eV smaller than the MCSTEP IP with the fully optimized MCSCF initial state.

3.2. H_2O

The SCF energy in the pVTZ basis is -76.0577 a.u.

We used a $(2a_1 3a_1 4a_1 1b_1 2b_1 1b_2 2b_2)$ CAS. There are 321 determinants for the initial state in this CAS. The converged MCSCF energy is -76.1506 a.u. The MCSCF reference state used in MCSTEP had the correct order of the Lagrangian eigenvalues. Hence, this MCSCF wavefunction was subsequently used as the initial state for our MCSTEP calculation.

Results are compared with the best reported EKT IPs [29] and experimental values [22, 23] in Table 2. For the three lowest IPs our MCSTEP results are in a very good agreement with experiment, differing from experiment by -0.41, -0.21, and 0.25 eV for $1b_1$, $3a_1$, and $1b_2$ IPs, respectively. The corresponding best reported EKT IPs differ from experiment by -0.27, 0.21, and 0.78 eV, respectively.

Table 1. The low lying vertical ionization potentials for HF in eV

Ion state	MCSTEP[a] pVTZ	MCSTEP[b] $\langle 5s3p1d/3s1p \rangle$	EKT[c] $\langle 5s3p1d/3s1p \rangle$	Exp.[d]
$(1\pi)^{-1}$	16.04	16.06	16.27	16.19
$(3\sigma)^{-1}$	19.97	20.10	20.35	19.9

[a] The basis set is the standard Dunning pVTZ set (Ref. [42]). The MCSCF complete active space CAS is $(3\sigma 1\pi 4\sigma 2\pi)$. One hundred and twelve determinants are present in the ground state MCSCF wavefunction

[b] The basis set is in the MESSKIT suite of codes [45] from Dunning [44]. The CAS is the same as in (a)

[c] The best reported EKT calculation in Ref. [29], 5180 terms were present in the neutral ground state wavefunction

[d] Ref. [21]

Table 2. The low lying vertical ionization potentials for H_2O in eV

Ion state	MCSTEP[a] pVTZ	EKT(Ψ^{II})[b] $\langle 5s3p1d/3s1p\rangle$	Exp.[c]
$(1b_1)^{-1}$	12.37	12.51	12.78
$(3a_1)^{-1}$	14.62	15.04	14.83
$(1b_2)^{-1}$	18.97	19.50	18.72

[a] The basis set is the standard Dunning pVTZ set (Ref. [42]). The MCSCF complete active space CAS is $(2a_1 3a_1 4a_1 1b_1 2b_1 1b_2 2b_2)$. There are 321 determinants in the MCSCF ground state

[b] The best reported EKT results in Ref. [29], 18 385 terms were included in the neutral ground state wavefunction

[c] Refs. [22, 23]

3.3. NH_3

The SCF energy in the pVTZ basis is -56.2183 a.u.

With the CAS $(1e3a_1 2e4a_1)$ there are 208 determinants in the reference state using this CAS. The eigenvalues of the Lagrangian of the converged MCSCF stationary point obtained with this CAS and basis set had an unwanted order. The correct order was obtained by excluding the $2a_1 \leftrightarrow 3a_1$ rotation. Subsequently, reintroducing that rotation again caused convergence to an MCSCF state with orbital energies in the unwanted order. Hence, the approximate MCSCF state (where the $2a_1 \leftrightarrow 3a_1$ rotation was excluded) was used in our MCSTEP calculation. The energy of the approximate MCSCF initial state is -56.2821 a.u.

MCSTEP IPs listed in Table 3 are compared with EKT IPs and experimental values [19, 20]. Our results are in a very good agreement compared with the experiment for the $(3a_1)^{-1}$ state differing by -0.22 eV and in an excellent agreement for $(1e)^{-1}$ state differing by only -0.08 eV. The best reported EKT IPs in Ref. [29] differed from experiment by -0.11 eV for the $(3a_1)^{-1}$ state and 0.29 eV for the $(1e)^{-1}$ state.

3.4. CH_4

The SCF energy in the pVTZ basis is -40.2133 a.u.

The CAS chosen was $(2a_1 1t_2 2t_2 3a_1)$. There are 313 determinants using this CAS for the neutral ground state. The MCSCF state with this CAS had the eigenvalues of the Lagrangian in the wanted order and the MCSCF energy is -40.2969 a.u. This MCSCF wavefunction was used as the initial state in our MCSTEP calculations.

In Table 4 we compare the MCSTEP results with the best EKT results [29] and experiment [25]. The MCSTEP IP for the lowest state is in excellent agreement with the experimental value, differing by -0.09 eV. The best reported EKT IP differs from experiment by 0.20 eV. (We do not report higher IPs since the next principal IP lies experimentally at 23.0 eV. For this system this is a larger value than for what we expect MCSTEP reliability – see above.)

Table 3. The low lying vertical ionization potentials for NH_3 in eV

Ion state	MCSTEP[a] pVTZ	EKT(Ψ^{II})[b] $\langle 5s3p1d/3s1p \rangle$	Exp.
$(3a_1)^{-1}$	10.58	10.69	10.8[c]
$(1e)^{-1}$	16.72	17.09	16.8[d]

[a] The basis set is the standard Dunning pVTZ set (Ref. [42]). The MCSCF complete active space CAS is ($1e3a_12e4a_1$). There are 208 determinants in the MCSCF ground state. No $2a_1 \leftrightarrow 3a_1$ rotation was included in the (approximate) MCSCF ground state

[b] The best EKT results reported in Ref. [29], 16 542 configurations were present in the ground state wavefunction

[c] Ref. [20]

[d] Ref. [19]

Table 4. The vertical ionization potentials for CH_4 in eV

Ion state	MCSTEP[a] pVTZ	EKT[b] $\langle 5s3p1d/3s1p \rangle$	Exp.[c]
$(1t_2)^{-1}$	14.31	14.60	14.40

[a] The basis set is the standard Dunning pVTZ set (Ref. [42]). The MCSCF complete active space CAS is ($2a_11t_22t_2$). There are 313 determinants in the MCSCF initial state

[b] The best EKT results reported in Ref. [29]. There were 43 194 terms in the ground state wavefunction

[c] Ref. [25]

3.5. N_2

The SCF energy in the pVTZ basis is -108.9806 a.u.

The CAS used is ($2\sigma_u3\sigma_g1\pi_u1\pi_g3\sigma_u$). This CAS has 396 determinants for the neutral ground state. The MCSCF initial state had the Lagrangian eigenvalues in the wanted order. The MCSCF energy is -109.1288 a.u. This wavefunction was used for the initial state for our subsequent MCSTEP calculations.

In Table 5 we compare the MCSTEP results in the pVTZ basis with the best reported EKT [29] and experimental IPs [22]. The $3\sigma_g$ and $2\sigma_u$ MCSTEP IPs are in excellent agreement with the experimental values, differing from the experimental values by 0.06 and -0.09 eV, respectively. The MCSTEP $1\pi_u$ IP differs from experiment by 0.31 eV.

For N_2 we also tried to duplicate the basis set reported in Ref. [29]. Again we were unable to exactly duplicate the basis set reported in Ref. [29]. With our $\langle 5s4p1d \rangle$ Dunning basis [44] obtained using the MESSKIT [45] suite of programs our SCF energy is -108.9759 a.u. The $\langle 5s4p1d \rangle$ basis in Ref. [29] had an SCF energy of -108.9780 a.u. With the same CAS as we used with the pVTZ basis our MCSCF energy in this basis is -109.1250 a.u. The eigenvalues of the MCSCF Lagrangian are in the wanted order for this basis set and CAS. Hence we used this wavefunction as an initial state for subsequent MCSTEP calculations.

Table 5. The vertical ionization potentials for N_2 in eV

Ion state	MCSTEP[a] pVTZ	MCSTEP[b] $\langle 5s4p1d\rangle$	EKT(Ψ^{IV})[c] $\langle 5s4p1d\rangle$	Exp.[d]
$(3\sigma_g)^{-1}$	15.66	15.62	15.66	15.60
$(1\pi_u)^{-1}$	17.29	17.28	17.22	16.98
$(2\sigma_u)^{-1}$	18.69	18.62	21.26	18.78

[a] The basis set is the standard Dunning pVTZ sets (Ref. [42]). The MCSCF complete active space CAS is $(2\sigma_u 3\sigma_g 1\pi_u 1\pi_g 3\sigma_u)$. There are 396 determinants in the MCSCF initial state

[b] The basis set is in the MESSKIT suite of codes [45] from Dunning [44]. The CAS is the same as in (a)

[c] The best EKT results reported in Ref. [29]. The ground state wavefunction has 34 721 terms

[d] Ref. [22]

With the $\langle 5s4p1d\rangle$ basis our MCSTEP IPs agreed even better with experiment than with the pVTZ basis. The $3\sigma_g$, $1\pi_u$, and $2\sigma_u$ IPs differed from experiment by 0.02, 0.30, and -0.16 eV, respectively. The best reported EKT IPs [29] differ from experiment by 0.06, 0.24, and 2.48 eV for the $3\sigma_g$, $1\pi_u$, and $2\sigma_u$ IPs.

3.6. *CO*

The SCF energy in the pVTZ basis is -112.7809 a.u.

The $(4\sigma 1\pi 5\sigma 2\pi 6\sigma)$ CAS was chosen. This CAS has 321 determinants for the neutral ground state. In order to obtain an initial state with the wanted order of the eigenvalues of the Lagrangian no $3\sigma \leftrightarrow 5\sigma$ rotation was included in the MCSCF optimization. The energy of this approximate MCSCF state is -112.8818 a.u. This state was used as the initial state in the subsequent MCSTEP calculations.

In Table 6 results are compared with experimental ionization potentials [22] and the best reported EKT calculations [29]. The 5σ and 4σ MCSTEP IPs are in excellent agreement with experiment, differing by only -0.02 and -0.08 eV. The 1π MCSTEP IP differs from experiment by 0.30 eV. The best reported EKT values differ from experiment by 0.09, 2.36, and 0.51 eV, respectively, for these IPs.

3.7. *HNC*

The SCF energy in the pVTZ basis set is -92.8928 a.u.

The CAS used was $(5\sigma 1\pi 6\sigma 2\pi)$. This CAS has 112 determinants for the neutral ground state. In order to obtain the wanted order of the Lagrangian eigenvalues the $4\sigma \leftrightarrow 5\sigma$ rotation was excluded from the initial state MCSCF optimization. This approximate MCSCF wavefunction was used in the MCSTEP calculations. The energy of this approximate MCSCF state was -92.9925 a.u.

In Table 7 results are compared with experimental [26] and the EKT ionization potentials. The lowest MCSTEP ionization potential is -0.29 eV different from experiment and the lowest EKT IP differs from experiment by 0.21 eV.

Table 6. The vertical ionization potentials for CO in eV

Ion state	MCSTEP[a] pVTZ	EKT(Ψ^{IV})[b] $\langle 5s3p1d\rangle$	Exp.[c]
$(5\sigma)^{-1}$	13.99	14.10	14.01
$(1\pi)^{-1}$	17.15	17.36	16.85
$(4\sigma)^{-1}$	19.70	22.14	19.78

[a] The basis set is the standard Dunning pVTZ set (Ref. [42]). The MCSCF complete active space CAS is $(4\sigma 1\pi 5\sigma 2\pi 6\sigma)$. There are 321 determinants in the MCSCF initial state. No $3\sigma \leftrightarrow 5\sigma$ rotation was included in the (approximate) MCSCF initial state

[b] The best EKT values reported in Ref. [29], 69 001 configurations were present in the initial state

[c] Ref. [22]

Table 7. The vertical ionization potentials for HNC in eV

Ion state	MCSTEP[a] pVTZ	EKT(Ψ^{II})[b] $\langle 3s2p1d/2s1p\rangle$	Exp.[c]
$(1\pi)^{-1}$	12.26	12.76	12.55
$(4\sigma)^{-1}$	14.22	—	—

[a] The basis set is the standard Dunning pVTZ set (Ref. [42]). The MCSCF complete active space CAS is $(5\sigma 1\pi 6\sigma 2\pi)$. There are 112 determinants present in the MCSCF initial state. No $4\sigma \leftrightarrow 5\sigma$ rotation was included in the (approximate) MCSCF initial state

[c] The best EKT results reported in Ref. [29], 1308 configurations were present in the ground state

[d] Ref. [26]

3.8. *HCN*

The SCF energy with the pVTZ basis set is -92.9085 a.u.

The $(5\sigma 1\pi 6\sigma 2\pi 7\sigma)$ CAS was chosen. This CAS has 321 determinants for the neutral ground state. To obtain the wanted order of the Lagrangian eigenvalues no $3\sigma \leftrightarrow 5\sigma$ rotation was included in the MCSCF optimization. The energy of this approximate MCSCF state is -93.0254 a.u. This state was used in the subsequent MCSTEP calculations.

The MCSTEP IPs are given in Table 8. They are in a very good agreement with experiment [27], differing by 0.16 and -0.20 eV to the $(1\pi)^{-1}$ and $(5\sigma)^{-1}$ states, respectively. The best reported EKT IPs [29] differ from experiment by 0.42 and 1.65 eV for $(1\pi)^{-1}$ and $(5\sigma)^{-1}$ states, respectively.

For this molecule we also performed large scale multireference configuration interaction (MRCI) calculations using the pVTZ basis and the same geometry in order to provide an additional comparison with MCSTEP. The Columbus package of codes was used [47]. In these calculations for each state of interest a full

Table 8. The vertical ionization potentials for HCN in eV

Ion state	MCSTEP[a] pVTZ	ΔMRSDCI + Q[b] pVTZ	EKT(Ψ^{II})[c] $\langle 3s2p1d/2s1p \rangle$	Exp.[d]
$(1\pi)^{-1}$	13.77	13.63	14.03	13.607
$(5\sigma)^{-1}$	13.81	13.78	15.66	14.011
$(4\sigma)^{-1}$	20.53	—	21.90	20.1[e]

[a] The basis set is the standard Dunning pVTZ set (Ref. [42]). The MCSCF complete active space CAS is $(5\sigma 1\pi 6\sigma 2\pi 7\sigma)$. There are 321 determinants present in the MCSCF initial state. No $3\sigma \leftrightarrow 5\sigma$ rotation was included in the (approximate) MCSCF ground state calculation

[b] For each state of interest the multireference CI used full valence CAS MCSCF orbitals; in addition to the MCSCF configurations, all single and double excitations were included from the valence orbitals to the unoccupied orbitals; quadrupole excitations were approximately included via a DV3 Davidson correction

[c] The best EKT results reported in Ref. [29], 8412 configurations were present in the ground state

[d] Ref. [27]

[e] Ref. [22]

valence CAS MCSCF calculation was first done. These orbitals and configurations and the configurations obtained by all possible single + double excitations from the valence orbitals in these configurations were used in the MRCI. Quadruple excitations were estimated via a DV3 Davidson correction [47, 48]. We label these as MRSDCI + Q. IPs were obtained by differencing MRSDCI + Q total electronic energies between the ground state neutral and each ionic state of interest (Δ). This procedure resulted with between 9 000 000 and 11 000 000 MRSDCI configurations for each state.

The ΔMRSDCI + Q IPs are 13.63 eV to the $(1\pi)^{-1}$ state and 13.78 eV to the $(5\sigma)^{-1}$ state. The corresponding MCSTEP IPs with this basis set are 13.77 and 13.81 eV, respectively.

3.9. C_2H_2

In the pVTZ basis, the SCF energy is -76.8498 a.u.

The CAS chosen was $(2\sigma_g 3\sigma_g 2\sigma_u 3\sigma_u 1\pi_u 1\pi_g)$ and the MCSCF energy is -76.9585 a.u. The eigenvalues of the MCSCF Lagrangian are in the wanted order so this MCSCF wavefunction was used as the initial state for MCSTEP.

Results compared with experimental values [25] and the best reported EKT IPs [29] are listed in Table 9. The MCSTEP ionization potential for $1\pi_u$ is in a very good agreement with the experiment, differing by 0.25 eV. The EKT IP to the $(1\pi_u)^{-1}$ state differs from experiment by -0.01 eV.

For all the other IPs listed in Table 9, the MCSTEP values are considerably closer to experiment than the EKT IPs. Since the difference between experiment and MCSTEP is slightly larger than we have usually attained, this may indicate that inclusion of the additional operators used in RMCSTEP is necessary to get very accurate $3\sigma_g$, $2\sigma_u$, and $2\sigma_g$ IPs.

Table 9. The vertical ionization potentials for C_2H_2 in eV

Ion state	MCSTEP[a] pVTZ	EKT(Ψ^{IV})[b] $\langle 5s3p1d/3s1p\rangle$	Exp.[c]
$(1\pi_u)^{-1}$	11.74	11.48	11.49
$(3\sigma_g)^{-1}$	17.26	18.11	16.7
$(2\sigma_u)^{-1}$	19.12	20.83	18.7
$(2\sigma_g)^{-1}$	25.50	27.51	23.5

[a] The basis set is the standard Dunning pVTZ set (Ref. [42]). The MCSCF complete active space CAS is $(2\sigma_g 3\sigma_g 2\sigma_u 3\sigma_u 1\pi_u 1\pi_g)$. There are 396 determinants in the MCSCF initial state

[b] The best EKT results reported in Ref. [29], 34721 configurations were included in the ground state

[c] Ref. [25]

3.10. H_2CO

In the pVTZ basis set the SCF energy is − 113.9113 a.u.

With the $(4a_1 5a_1 6a_1 1b_1 2b_1 2b_2 3b_2)$ CAS the MCSCF energy is − 114.0250 a.u. The eigenvalues of the MCSCF Lagrangian are in the wanted order; hence, this MCSCF wavefunction was used as the initial state in MCSTEP.

Table 10 lists the results compared with the experimental ionization potentials [30] and the best reported EKT results [29]. For the three lowest states, MCSTEP IPs are in very good agreements with experiment, differing by − 0.16, 0.21, and 0.23 eV for $2b_2$, $1b_1$, and $5a_1$ IPs, respectively. For these three IPs the best reported EKT IPs differ from experiment by 0.43, 0.74, and 1.41 eV, respectively.

For the remaining two IPs reported in this table, the MCSTEP values are not as close to experiment; however, they are considerably closer to the experimental values than are the EKT IPs. For these two higher lying IPs perhaps a procedure such as RMCSTEP [15], which includes contributions from ionization processes where an electron is removed and one of the remaining electrons is excited to a diffuse orbital, is necessary to attain even more accurate IPs (see above).

3.11. B_2H_6

In the pVDZ basis set the SCF energy is − 52.8157 a.u.

A $(3a_g 4a_g 3b_{1u} 1b_{3u} 1b_{2u} 1b_{2g} 1b_{3g})$ CAS was used. The MCSCF energy is − 52.8506 a.u. and the eigenvalues of the MCSCF Lagrangian are in the wanted order. This MCSCF wavefunction was used as the initial state in the MCSTEP calculations.

Table 11 lists the results compared with the experimental ionization potentials [31] and the best reported EKT results [29]. For the four lowest states, our MCSTEP results are in very good agreement with experiment, differing between 0.07 and 0.35 eV from experiment. The EKT results are considerably worse, differing from experiment by 0.41–0.68 eV.

The last two MCSTEP IPs listed in Table 11 do not agree as well with experiment; however, agreement is considerably better than for the EKT IPs. As for the three highest IPs reported above for C_2H_2 and the highest two IPs reported for

Table 10. The low lying vertical ionization potentials for H_2CO in eV

Ion state	MCSTEP[a] pVTZ	EKT($\Psi^{\rm I}$)[b]	EK$^{\rm I}$($\Psi^{\rm II}$)[b] $\langle 3s2p1d/2s1p\rangle$	Exp.[c]
$(2b_2)^{-1}$	10.74	11.33	11.00	10.9
$(1b_1)^{-1}$	14.71	15.24	15.00	14.5
$(5a_1)^{-1}$	16.33	18.03	17.51	16.1
$(1b_2)^{-1}$	17.50	18.31	18.20	17.0
$(4a_1)^{-1}$	22.31	23.51	23.32	21.4
$(3a_1)^{-1}$	34.88	38.46	38.24	34.2

[a] The basis set is the standard Dunning pVTZ sets (Ref. [42]). The MCSCF complete active space CAS is $(4a_1 5a_1 6a_1 1b_1 2b_1 2b_2 3b_2)$. There are 321 determinants present in the MCSCF initial state

[b] The best reported EKT results reported in Ref. [29]. There were 1308 configurations in the ground state

[c] Ref. [30]

Table 11. The low lying vertical ionization potentials for B_2H_6 in eV

Ion state	MCSTEP[a] pVDZ	EKT[b] $\langle 3s2p1d/2s1p\rangle$	Exp.[c]
$(1b_{3g})^{-1}$	12.19	12.59	11.9
$(3a_g)^{-1}$	13.85	14.12	13.5
$(1b_{2u})^{-1}$	13.97	14.59	13.9
$(1b_{3u})^{-1}$	15.03	15.21	14.8
$(2b_{1u})^{-1}$	16.78	17.18	16.1
$(2a_g)^{-1}$	23.24	24.36	21.3

[a] The basis set is the standard Dunning pVTZ sets (Ref. [42]). The MCSCF complete active space CAS is $(3a_g 4a_g 3b_{1u} 1b_{3u} 1b_{2u} 1b_{2g} 1b_{3g})$. There were 165 determinants in the ground state

[b] The best reported EKT results in Ref. [29], 1844 configurations were included in the neutral ground state

[c] Ref. [31]

H_2CO, it appears that a procedure such as RMCSTEP may be necessary to achieve very accurate IPs for the two highest IPs in B_2H_6.

4. Summary and conclusions

With the multiconfigurational spin tensor electron propagator method (MCSTEP) ionization energies are obtained directly rather than by separately performing total electronic energy calculations on the neutral initial state and on each of the ion states of interest. This method has been previously successfully applied to both closed [14–16, 36–38] and open shell [16, 17, 32–36] (initial state) systems.

In this paper, we presented calculational results of MCSTEP ionization potentials for the many electron systems HF, H_2O, NH_3, CH_4, N_2, CO, HNC, HCN, C_2H_2, H_2CO, and B_2H_6. We have chosen these molecules since the low-lying IPs on these were recently determined using the extended Koopmans' theorem method (EKT) so that comparisons with MCSTEP can be made. MCSTEP IPs in this paper are compared both with experimental values and extended Koopman's theorem calculations.

Previous MCSTEP calculations used a fully optimized MCSCF initial state. In this paper we demonstrated that initial states where one rotation is excluded in the MCSCF optimization can also provide reliable and accurate MCSTEP IPs. These approximate MCSCF states are used as the MCSTEP initial state when the eigenvalues of the Lagrangian of the fully optimized MCSCF state are in an unwanted order. (When the Lagrangian eigenvalue ordering is incorrect MCSTEP IPs may not be as reliable.) Use of approximate MCSCF states in MCSTEP may be particularly important especially for larger systems where a full valence CAS MCSCF is impractical or even impossible.

The MCSTEP results reported here further demonstrate the applicability and reliability of MCSTEP for the lower-lying IPs of small molecules. Comparison with experiment demonstrates that accurate and reliable IPs are attained with relatively small active spaces.

To obtain fairly accurate EKT results, large active spaces are required [29]. Although we could not exactly reproduce the EKT basis sets of Ref. [29], our calculations with similar basis sets show that MCSTEP IPs obtained using fairly small CAS spaces are usually better, particularly for the low-lying IPs above the lowest IP.

However, it should also be noted that since no transfer operators are present in EKT calculations, it is a simple matter to calculate EKT IPs once the initial state is obtained. While it is also not particularly difficult to determine MCSTEP IPs (i.e. typically matrices no larger than 400 × 400 are needed), it is still more complicated than the EKT method.

Because of the operators used in EKT only low-lying principal IPs can be obtained with EKT. With MCSTEP only the lowest few IPs of each symmetry can also be accurately obtained. Because of the use of transfer operators in MCSTEP more of these lower lying IPs can be reliably determined than with EKT.

As mentioned previously, to accurately determine even higher-lying principal as well as shake-up IPs requires the inclusion of operators that allow for electron removal along with excitation of the remaining electrons into diffuse orbitals [15, 33, 34, 38]. These are not present among the operators used in MCSTEP or in EKT. (Note that the MCSTEP transfer operators allow only for excitation within the valence orbitals but not to diffuse orbitals which are present only among the unoccupied MCSCF orbitals when a basis set which includes diffuse functions is used.) We have previously included these additional operators in a theory known as repartitioned MCSTEP (RMCSTEP) [15].

Work is continuing in our laboratory on improving MCSTEP, for example, by incorporating into the method a form of multiconfigurational perturbation theory. We hope to report on these methods in the near future.

Acknowledgments. Danny L. Yeager and Dodi Heryadi would like to acknowledge support for this research in part from The Robert A. Welch Foundation Grant No. A-770. Acknowledgment is made to donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also especially thank Professor Jack Simons for providing the MESSKIT suite of codes which we used to obtain MCSCF wave functions and Dr. Ron Shepard for providing us with the GUGA multireference CI code (Columbus Package).

In addition we particularly wish to acknowledge and thank Prof. Jan Linderberg. DLY has spent many delightful times at dinners and parties at the Linderberg home and has enjoyed many insightful scientific discussions with Jan. All of us have intellectually profited immensely from reading his book and papers.

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