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Calculation of Molecular Ionization Potentials Using Single- and Multireference Coupled-Cluster Methods. Application to Methyleneamine, CH_2NH, and Methylenephosphine, CH_2PH[†]

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Abstract: Two recently developed coupled-cluster (CC) schemes, quasi-restricted Hartree–Fock CC (QRHF-CC) and multireference CC (MR-CC), which are expected to be capable of calculating molecular ionization potentials (IPs) to a high accuracy, have been compared with each other, with conventional single-reference CC schemes (CCSD and CCSDT-1), with other theoretical techniques, and with experiment by calculating the vertical valence IPs of the important isovalent transients methyleneamine, CH_2NH, and methylenephosphine, CH_2PH. In addition, we report results for P_2 to assess the quality of the P basis set. Several different basis sets are considered. The QRHF-CC and MR-CC schemes give very similar results, which are in excellent agreement with the CCSDT-1 approach, when the latter is applicable. At the highest level, agreement with experiment is excellent, with mean errors of less than 0.2 eV. The influence of triple-excitation effects in the MR-CC and QRHF-CC methods on IPs is considered.

There are currently several schemes that are capable of calculating the ionization potentials (IPs) of a molecule with high accuracy. These methods can be broadly grouped into three categories.

There are the configuration interaction (CI) methods.[1] Separate CI calculations are carried out on the molecule and the cationic states of interest, and the IPs are obtained by taking the differences of the molecular and cationic energies.

The second group of methods is based on Green's function or, equivalently, electron propagator techniques.[2–5] A distinguishing feature of these methods is that the IPs are obtained directly (as the poles of the single-particle Green's function), rather than as the difference of two separately calculated energies. These methods have been applied to a very large number of systems,[2–6] and with extended basis sets are capable of high accuracy.

Finally, there are methods based on the coupled-cluster (CC) approach,[7] which includes many-body perturbation theory (MBPT) as a special case.[7a,8] Conventionally, these methods would obtain the IPs of a molecule by carrying out separate CC calculations on the molecule and cations and would use a UHF reference function for the open-shell states, with attendant spin contamination. The links between CC and Green's function approaches have been discussed.[9]

Recently, two new CC schemes for determining molecular IPs have been developed. The first of these is termed the quasi-restricted Hartree–Fock CC (QRHF-CC) method.[10] This method uses the same set of RHF orbitals in all calculations, and for IP calculations these are normally the neutral molecule SCF orbitals, subject to maximum double occupancy, making the reference function an eigenfunction of spin. This is to be compared with the conventional CC (and CI) approaches in which different sets of HF orbitals are obtained for each state. The use of a single set of orbitals gives the QRHF-CC method the advantage of being able to treat, at least in principle, several cationic states of a given symmetry. This differs from conventional CC and CI methods that would normally be restricted to the lowest state of a given symmetry because of variational collapse in the HF procedure. A potential disadvantage of using a single set of orbitals for all states is that some states might be described less well than others and that additional CC diagrams, which are zero when HF orbitals are used, must be evaluated. However, the latter does not present a problem since these terms are computationally no more expensive to evaluate than the HF-CC terms, and our ACES code[11] was originally written to handle CC calculations with non-HF orbitals for open- and closed-shell systems.[12] The former problem is largely ameliorated by CC theory since orbital rotations are effectively built into the CCSD theory by virtue of the $\exp(T_1)$ operator.[13] Furthermore, unlike UHF-based methods, QRHF-CC approaches retain the spin eigenfunction property for the projected value of $\hat{S}^2$, i.e. $\langle \Phi_0 | \hat{S}^2 \exp(T) | \Phi_0 \rangle = S(S + 1)$, and having the orbitals the same for all states facilitates the evaluation of transition moments. Alternatively, high-spin ROHF orbitals could be used for the open-shell states,[10] but as in the UHF approach, they would be different for different states. It should be mentioned that a single set of orbitals for all states is implicit in propagator methods and has also been proposed in perturbation methods[14,15] but for

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Table I. Microwave Geometries of CH_2NH[24b] and CH_2PH[34b,a]

r(C=N)	1.273	∠H′CN	117.9
r(C—H′)	1.090	∠H″CN	125.1
r(C—H″)	1.090	∠HNC	110.4
r(N—H)	1.021		
r(C=P)	1.673	∠H′CP	118.4
r(C—H′)	1.090	∠H″CP	124.4
r(C—H″)	1.090	∠HPC	97.4
r(P—H)	1.420		

[a] H′ is trans (and H″ is cis) to the hydrogen attached to the nitrogen/phosphorus atom. Bond lengths are in angstroms, and bond angles, in degrees.

CC methods has only recently been exploited for the calculation of excited-state energies[16] and IPs.[10]

The second new CC scheme suitable for the calculation of molecular IPs is a multireference CC (MR-CC) approach.[17-19] Building upon some aspects of earlier work in this area,[17] methods have recently been developed by Pal et al.[18] and by Haque and Kaldor.[19] These schemes are suitable for calculating the IPs, electron affinities (EAs), excitation energies (EEs), double ionizations, etc. Each scheme leads to a hierarchical system of CC equations. Initially, a standard CC calculation on the closed-shell molecule is performed. After this the IP, EA, EE, etc. CC problems are successively solved. These calculations are efficient as they require only the additional solution of the CC equations for the limited number of new correlation terms that arise for the particular energy difference.[18,19] Noteworthy features of the methods are that a single set of orbitals, usually the closed-shell molecule HF orbitals, is used throughout; and several IPs, EAs, EEs, etc. are obtained, directly, in a single calculation.

With these new developments CC methods are potentially poised to play an important role in photoelectron spectroscopy. Although refinements and extensions will continue to be made,[20] the existing methods seem to be sufficiently accurate, and the computer codes sufficiently well developed, for us to embark on applications.

In this paper we employ the QRHF-CC scheme[10] and the MR-CC scheme[18] to calculate the vertical valence IPs of methyleneamine (methylenimine) CH_2NH, and methylenephosphine, CH_2PH. We compare the results with data obtained from conventional single-reference CC and MBPT(4) calculations, from other theoretical methods, and from experiment. The first objective of this work is to compare the QRHF-CC and MR-CC methods with each other and with the more established CC schemes and to assess how well the various CC techniques can calculate molecular IPs.

At the time this paper was submitted, the photoelectron spectrum of methylenephosphine had not been published,[21] and so another aim of this work was to provide a prediction of the valence IPs of this important molecule. While this paper was being reviewed, however, the work of Lacombe et al.[22] appeared, presenting for the first time the photoelectron spectrum of methylenephosphine. This work suggested that previous theoretical calculations on CH_2PH seriously underestimate the separation between the first and second IPs of this molecule, and this point is addressed, including an additional study of P_2 to assess potential basis set effects.

Finally, although there have been several theoretical calculations of the IPs of CH_2NH and CH_2PH (see below), only one study of CH_2NH obtained more than the first two IPs, but only a double-ζ basis set was employed, while the third and fourth IPs of CH_2PH have never previously been calculated.

Methylenimine was first suggested as a possible reaction intermediate as long ago as 1917.[23] Since then, it has received much experimental[24-28] and theoretical[29-32] attention. Of particular relevance to the present work are three determinations of the photoelectron spectrum[26-28] and some IP calculations.[30-32] Bruna et al.[30] have reported calculations of the lowest two IPs by the CI method. A Green's function study, giving estimates of all the IPs but with only a double-ζ basis set, has been carried out by von Niessen et al.[31] Finally, Frost et al.[32] have computed the valence IPs using the semiempirical HAM/3 method.

Methylenephosphine was first detected in 1976.[33] Later, more comprehensive studies[34,35] confirmed this more tentative first sighting. The spectroscopic detection of methylenephosphine has spawned a huge interest in the phosphaalkenes in the last decade or so.[22,36-38] The photoelectron spectra of three simple phos-

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phaalkenes, methylenephosphine,[22] 1-phosphapropene,[22] and 2-phosphapropene,[36m] have been reported. There have been two correlated calculations of the first two IPs of methylenephosphine.[22,30] The question of the nature of the highest occupied orbitals of the phosphaalkenes has been addressed by several other groups,[36j,k,m,37h,38a,b,e,g,i,j] although much of this work has relied on Koopmans' theorem.

In the next section we give details of our calculations. Following that, we discuss and compare the results obtained with the different methods and basis sets and with experiment.

Computational Details

The calculations on CH_2NH are carried out at the microwave geometry of Pearson and Lovas,[24b] and those on CH_2PH at the microwave geometry of Kroto, Nixon, and Ohno.[34b] The two geometries are shown in Table I.

Four different Gaussian basis sets are used in this work, a double-ζ (DZ), a double-ζ plus polarization (DZP), a triple-ζ valence plus polarization (TZP), and, for CH_2PH only, an extended set (EXT), containing diffuse functions on P and multiple polarization functions on C and P. The DZ basis sets for H, C, N, and P are, respectively, Dunning's 2s and 4s2p contractions of 4s and 9s5p primitive sets[39] and Dunning and Hay's 6s4p contraction of an 11s7p primitive set.[40] The TZ basis sets for H, C, N, and P are Dunning's 3s and 5s3p contractions of 5s and 10s6p primitive sets[41] and McLean and Chandler's 6s5p contraction of a 12s9p primitive set.[42] The DZP and TZP sets use polarization exponents of 1.0, 0.75, 0.8, and 0.5 for H, C, N, and P. The EXT set for CH_2PH comprises the TZ set augmented with diffuse s and p functions on P (exponents 0.04 and 0.03, respectively[6b]), three polarization functions on P (exponents of 0.15, 0.45, and 1.5[6b]), two polarization functions of C (exponents 0.375 and 1.5), and a single polarization function on H having exponent 1.0.

Three sets of calculations are reported:

(i) Standard single-reference MBPT(4),[7a] CCSD,[7b] and CCSDT-1[7c] calculations on the neutral molecules and the lowest A′ and A″ states of the cations. We denote these methods collectively HF-MBPT/CC, the prefix HF emphasizing that these calculations use HF orbitals for each electronic state considered (UHF orbitals for open-shell states).

(ii) MR-CCSD calculations[18] and selected MR-CC calculations used to assess the effect of the inclusion of triple excitations on the IPs of CH_2PH. The starting point is a CCSD calculation on the neutral molecule, and neutral molecule RHF orbitals are used to describe the N-1 electron states. The two methods including the effects of triple excitations are denoted MR-CCSD + T(3) and MR-CCSD + T*(MR-CCSD + T*(3)) and are defined elsewhere.[43]

Table II. Comparison of Valence IPs of CH_2NH Calculated by CC-Based Methods (DZP Basis Set)[a]

orbital	MBPT(4)	CCSD	CCSDT-1	QRHF-CCSD	QRHF-CCSDT-1	MR-CCSD
5a′	10.63	10.37	10.39	10.40	10.43	10.28
1a″	12.29	12.15	12.26	12.14	12.28	12.25
4a′				15.17	15.11	15.07
3a′				17.32	17.14	17.18

[a] The units are electronvolts.

(iii) QRHF-CCSD and QRHF-CCSDT-1 calculations[10] on the neutral molecule and the valence electronic states of the cations. These calculations also use neutral molecule RHF orbitals but construct a single-reference function for each state by appropriate occupation of the RHF orbitals subject to maximum double occupancy. Thus, the reference function is an eigenfunction of spin.

The different methods are compared using DZP basis sets. To examine the effects of basis set on the calculated IPs, MR-CCSD calculations are carried out using a variety of basis sets. All the data we report are from frozen-core calculations. The effect of freezing the core on the valence IPs is very small, no more than 0.02 eV. All the calculations are performed with the ACES program system.[11]

Results and Discussion

Although CH_2NH and CH_2PH are isovalent, their electronic structures are very different. Formally assigning 12 valence electrons to each molecule, their valence electronic configurations are, respectively, 1a′2a′3a′4a′1a″5a′ and 1a′2a′3a′4a′5a′1a″. The 1a′ and 2a′ ionizations are too high in energy to be observed in the usual He I photoelectron experiment, but for both molecules the other four principal ionizations have been observed. The HOMO of CH_2NH is predominantly of nitrogen lone-pair character and is well separated from the C–N π orbital (1a″). For CH_2PH the HOMO is the C–P π orbital, which is quite close in energy to the P lone-pair orbital (5a′). The energy difference is sensitive to substitution, which may be reflected in the fact that coordination to transition metals may be through either the lone pair or the π orbital,[37] although the vast majority of examples feature lone-pair coordination.

We consider each of the two molecules separately and then, in the light of these results, consider the relative accuracy and applicability of the QRHF-CC and MR-CC schemes.

A. CH_2NH. We compare the data obtained with the HF-MBPT/CC, QRHF-CC, and MR-CCSD methods. In Table II we show the IPs of the CH_2NH calculated by the MBPT(4), CCSD, CCSDT-1, QRHF-CCSD, QRHF-CCSDT-1, and MR-CCSD methods. For the HF-MBPT/CC methods we are limited to only the two lowest energy IPs. For the QRHF-CC and MR-CCSD methods we report the four lowest energy IPs.

Although the purpose of the HF-MBPT/CC calculations is to assess the accuracy of the QRHF-CC and MR-CCSD results, they do have some interest in their own right. We note first the different behavior of the MBPT(4) and CCSDT-1 methods. The data for the 1a″ orbital are in line with previous observations,[44] namely that when a system is well described by a single-reference function, low-order MBPT and CC approaches give similar results. For the 5a′ orbital, however, the two methods give quite different results. Apparently, the reason for this is that the UHF wave function for the lowest A′ state of the cation is seriously spin contaminated ($2S + 1 = 2.45$, at the UHF level), and this causes the MBPT energy to be poor, while the CC iterations remove most of the spin contamination ($2S + 1 = 2.06$, for the final CC wave function).[45] Even starting from a seriously spin-contaminated wave function, the CCSD method can obtain good results since it benefits from the natural annihilation of the first contaminating spin components.[46]

The other point of interest in the HF-MBPT/CC data is the difference between the CCSD and CCSDT-1 results for the 1a″

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Table III. Comparison of Valence IPs of CH_2NH Calculated by the QRHF-CCSDT-1, MR-CCSD, Green's Function (GF), and CI Methods[a]

orbital	QRHF-CCSDT-1	MR-CCSD	GF	CI(i)	CI(ii)
5a′	10.43	10.28	10.09	10.52	10.44
1a″	12.28	12.25	12.32	12.26	12.21
4a′	15.11	15.07	15.27		
3a′	17.14	17.18	17.65		

[a] The GF data are from von Niessen et al.,[31] and the CI data from Bruna et al.[30] The units are electronvolts.

IP. Evidently, connected triple excitations are necessary to describe this ionization accurately.

Comparing now the QRHF-CC and MR-CCSD data with the CCSD and CCSDT-1 results, we see that the methods are for the most part in good agreement. The good agreement between the QRHF-CCSD and CCSD data and between the QRHF-CCSDT-1 and CCSDT-1 data confirm the effectiveness of exp(T_1) in accounting for orbital relaxation effects.[13] For the 1a″ IP we see that the MR-CCSD and QRHF-CCSDT-1 methods are in perfect agreement with the CCSDT-1 data. The QRHF-CCSD result is in poorer agreement presumably because of the lack of connected triple excitations in this model. It is noteworthy that while the MR-CCSD method does not explicitly include connected triple excitations, it appears to be able to account partly for their effects, as one would expect, based upon the argument that single and double excitations from a multireference space of N-1 electrons would tend to introduce certain additional effects that one might tend to call "triples" relative to a single-reference function. However, due to the different numbers of electrons involved, the concept of triples is different for the MR-CCSD approach, compared with the ordinary single-reference triples. This is emphasized for the 5a′ IP, where the MR-CCSD result does not agree so well with the QRHF-CCSDT-1 or CCSDT-1 data. Indeed, for this IP the QRHF-CCSD value is in better agreement with experiment SS (Table IV). The reason for this is not clear, but contrary to the multireference argument given above, certain other correlation effects present in QRHF-CCSD would correspond to "triple-excitation" effects in the MR-CC scheme.[43] In some cases, such as N_2, they play an important role.[43] For the other two IPs, the MR-CCSD and QRHF-CCSDT-1 results are very close. The QRHF-CCSD result for the 4a′ IP is good, but for the 3a′ IP it differs from the QRHF-CCSDT-1 result by over 0.2 eV, which may be unambiguously attributed to triple excitations.

We now compare the MR-CCSD and QRHF-CCSDT-1 data with results obtained with other theoretical techniques. In Table III we show the MR-CCSD and QRHF-CCSDT-1 data along with the CI data of Bruna et al.[30] and the Green's function data of von Niessen et al.[31] The CI calculations of Bruna et al.[30] were carried out using a DZP basis set similar to ours. These workers report IPs determined (1) from MRD-CI calculations and (2) by adding a multireference Langhoff–Davidson correction term to the MRD-CI energies. The correction is intended to account approximately for the effects of excitations not present in the MRD-CI wave function. The first column of CI IPs in Table III is from MRD-CI energies, and the second column from the corrected energies.

The data of von Niessen et al. were obtained using a basis set without polarization functions and so cannot be expected to be of very high accuracy. These workers report estimates of all the principal IPs. Our data are not in particularly good agreement with their results, presumably because of the difference in basis sets. For the 5a′ IP our QRHF-CCSDT-1 result is in very good agreement with the corrected MRD-CI value. The difference of 0.08 eV between the two CI results should be an indication of the importance of quadruple excitation effects beyond those taken account of in the MRD-CI procedure but rigorously introduced in CC methods because of the presence of $T_2{}^2/2$. The large difference between the two CI estimates shows that the good agreement of the MRD-CI estimate of the 5a′ IP with experiment (see Table IV) is likely to be fortuitous. For the 1a″ IP there is very good agreement between the QRHF-CCSDT-1, MR-CCSD, and MRD-CI results, while the corrected MRD-CI IP is somewhat lower than these.

Table IV. Comparison of MR-CCSD Valence IPs of CH_2NH for Three Different Basis Sets with the Experimental Data of Peel and Willett[26] (PW), Bock, Dammel, and Horner[27] (BDH), and Schulz and Schweig[28] (SS)[a]

	MR-CCSD			experiment		
orbital	DZ	DZP	TZP	PW	BDH	SS
5a′	9.72	10.28	10.37	10.52	10.70	10.56
1a″	12.33	12.25	12.32	12.43	12.48	12.44
4a′	14.96	15.07	15.13	15.13	15.11	15.00
3a′	17.21	17.18	17.25	17.04	17.07	17.00

[a] The units are electronvolts.

Table V. Comparison of Valence IPs of CH_2PH Calculated by CC-Based Methods (DZP Basis Set)[a]

orbital	MBPT(4)	CCSD	CCSDT-1	QRHF-CCSD	QRHF-CCSDT-1	MR-CCSD
1a″	10.05	9.91	10.03	9.90	10.05	10.07
5a′	10.64	10.24	10.25	10.22	10.24	10.29
4a′				13.15	13.15	13.18
3a′				15.15		15.13

[a] The units are electronvolts.

Finally, in Table IV we compare our MR-CCSD data for DZ, DZP, and TZP basis sets with the experimental data of Peel and Willett,[26] of Bock, Dammel, and Horner,[27] and of Schulz and Schweig.[28] The agreement between our best results and experiment overall is very good, being almost competitive with the variance of the experimental results. Depending upon the experimental value one selects, the TZP 5a′ IP is in error by 0.15–0.33 eV. That this IP is difficult to calculate accurately is not surprising since the 5a′ orbital is of predominantly nitrogen lone-pair character, and one would therefore anticipate that a large basis set would be required. Certainly, the difference between the DZP and TZP estimates suggests that further basis set improvements will bring the theoretical value into better agreement with experiment. It should also be noted that the CCSDT-1 estimate of the 5a′ IP is in closer agreement with experiment than the MR-CCSD estimate so that basis set incompleteness is probably not the only cause of the difference between the MR-CCSD data and experiment. As we mentioned above, this may be an instance where extension of the MR-CC model to include additional triple-excitation effects is needed. The agreement between the MR-CCSD values for the 1a″ and 4a′ IPs is very good. For the TZP basis set the differences are 0.11–0.16 and 0.00–0.13 eV, respectively. For the 3a′ IP the agreement is not quite so good, giving a difference of 0.18–0.25 eV. However, in view of the basis set dependence of the MR-CC value for this IP and the QRHF-CCSDT-1 estimate (Table II), it is conceivable that the experimental estimates are slightly too low. In addition, overestimation of the IP implies that the calculations describe the ion better than the neutral molecule, which would be contrary to normal expectations.

B. CH_2PH. As for CH_2NH, we first compare the results obtained from the HF-MBPT/CC methods with the results of the QRHF-CC and MR-CCSD methods. The relevant data are shown in Table V. For the HF-MBPT/CC methods we calculate only the first two IPs. With the MR-CCSD and QRHF-CCSD approaches we obtain the lowest four valence IPs, and with the QRHF-CCSDT-1, the three lowest. Convergence difficulties prevent us from obtaining the higher energy valence IPs when using the QRHF-CCSDT-1 method. This is an indication that these states have substantial multireference character, for which the single-reference QRHF-CC method is less suited. The MR-CC approach has no such problem but would have to consider additional active orbitals to obtain the higher energy ionizations.

To a large extent, the results for CH_2PH parallel those for CH_2NH. Thus, (1) the MBPT (4) and CCSDT-1 values for the 1a″ IP are similar yet for the 5a′ IP are markedly different

Table VI. Comparison of Valence IPs of CH_2PH Calculated by the QRHF-CCSDT-1, MR-CCSD, and CI Methods[a]

orbital	QRHF-CCSDT-1	MR-CCSD	CI(i)	CI(ii)	CI(iii)
1a″	10.05	10.07	10.09	10.11	10.02
5a′	10.24	10.29	10.30	10.29	10.19
4a′	13.15	13.18			
3a′		15.13			

[a] The first and second sets of CI data are from Bruna et al.,[30] and the third is from Lacombe et al.[22] The units are electronvolts.

Table VII. Comparison of MR-CCSD Valence IPs of CH_2PH for Four Different Basis Sets with the Experimental Data of Lacombe et al.[22]

	MR-CCSD				
orbital	DZ	DZP	TZP	EXT	experiment
1a″	10.18	10.07	10.08	10.18	10.30
5a′	9.82	10.29	10.27	10.42	10.70
4a′	13.14	13.18	13.19	13.27	13.20
3a′	15.08	15.13	15.16	15.25	15.00

[a] The units are electronvolts.

presumably because of spin contamination ($2S + 1$ is 2.44 for the initial UHF function and 2.10 for the converged CC function), (2) connected triple excitations are important in the calculation of the 1a″ IP, and (3) the QRHF-CC approaches give results in perfect agreement with those from the HF-CC approaches. There is almost perfect agreement between the 5a′ IPs calculated by the QRHF-CCSDT-1, CCSDT-1, and MR-CCSD methods, while as discussed above, for CH_2NH the MR-CCSD method gives a significantly lower 5a′ IP than do the two CCSDT-1 methods. As for CH_2NH, the MR-CCSD, CCSDT-1, and QRHF-CCSDT-1 values for the other IPs are also in good agreement. A second difference is that for CH_2PH the QRHF-CCSD method gives a value for the 3a′ IP, which is in excellent agreement with the value given by the MR-CCSD method and which is not the case for CH_2NH.

Next we compare the MR-CCSD and QRHF-CCSDT-1 data with the CI results of Bruna et al.[30] and of Lacombe et al.[22] As for CH_2NH, Bruna et al. used a DZP basis set and obtained only the lowest two IPs. Lacombe et al. used pseudopotentials and a DZ valence basis set augmented with a polarization function and a diffuse s function on P. They used an approximate multireference CI procedure (CIPSI) and evaluated various approximate corrections to this model. In Table VI we show our MR-CCSD and QRHF-CCSDT-1 data along with the CI data of Bruna et al. and Lacombe et al. The latter report estimates of the first two IPs given by several different methods, but since for all but one method the order of the IPs is wrong, we give only one pair of their calculated IPs.

Unlike for CH_2NH, the MRD-CI and corrected MRD-CI data are in good agreement. The agreement between the CI results of Bruna et al. and our CC results is also good. The CI results of Lacombe et al. are in reasonable agreement with our data.

Finally, we look at basis set effects on the MR-CC IPs of CH_2PH and compare with the experimental data of Lacombe et al.[22] In Table VII we show data for our DZ, DZP, TZP, and EXT basis sets. As noted, for example, by von Niessen et al.,[6] a DZ basis set may give an incorrect ordering of IPs for systems containing second-row atoms, and this is the case here. Although there is little difference in the results given by the DZP and TZP basis sets, extending the basis set by adding diffuse functions and more polarization functions has a significant effect on the calculated IPs. Again, the importance of these basis set improvements has been noted by von Niessen et al.[6]

Comparing our results with the experimental data, we see that the EXT basis set gives a considerably improved description compared with the DZP and TZP sets, except for the 3a′ orbital. With the EXT basis set the errors are 0.12, 0.28, 0.07, and 0.25 eV for the 1a″, 5a′, 4a′, and 3a′ IPs, respectively.

Table VIII. Two Lowest Energy IPs of P_2 As Determined by the MR-CCSD Method with the EXT Basis Set, by Green's Function Methods Using Several Different Basis Sets,[6b] and by Experiment[47] [a]

	GF				MR-CCSD:	
	I[b]	II[b]	III[b]	IV[b]	EXT[b]	expt
$1\ \pi_u$	10.36	10.34	10.32	10.41	10.54	10.62
$2\ \sigma_g$	9.93	10.61	10.64	10.67	10.72	10.81

[a] The units are electronvolts. [b] Bases I–IV used by von Niessen et al.[6b] are, respectively, as follows: (12s9p/6s4p), (12s9p2d/6s4p2d), (12s9p3d/6s4p3d), and (13s10p2d/7s5p2d). For comparison, our EXT basis set is (13s10p3d/7s5p3d).

Table IX. Investigation of the Effect of the Addition of Some Triple-Excitation Effects to the MR-CCSD Model on the IPs of CH_2PH (DZP Basis Set)[a]

orbital	MR-CCSD	MR-CCSD + T(3)	MR-CCSD + T*(3)
1a″	10.07	10.00	9.98
5a′	10.29	10.32	10.28
4a′	13.18	13.26	13.19
3a′	15.13	15.41	15.27

[a] The units are electronvolts.

The major failure of all the basis sets and other theoretical calculations[22,30] lies in the splitting of the first two IPs. The experimental value is 0.40 eV, and our best estimate of this is 0.24 eV. Noting that with the EXT basis set the error for the 5a′ IP is considerably larger than that for the 1a″ IP, it would seem that the main source of error is in the description of the P lone-pair orbital. At this point it is pertinent to emphasize that the P basis set we have used would seem to be of high quality. To illustrate this, we note, first, that the SCF energy of P_2 with this basis set is −681.481 127 au, which is significantly lower than any of the energies given by the basis sets used by von Niessen et al.[6b] Second, we have used this basis set to calculate the first two IPs of P_2 using the MR-CCSD method. In Table VIII we show these results along with Green's function data of von Niessen et al.[6b] and the experimental IPs of Bulgin et al.[47] The very good agreement between our results and experiment gives further evidence that our basis set is of high quality, as well, of course, as evidence for the accuracy of the MR-CCSD method. von Niessen et al.[6b] did not simultaneously use both diffuse functions and three sets of polarization functions, otherwise their results would be expected to be of similar accuracy to ours. So while further basis set extension might be important and should be investigated, other factors might be partly responsible for the remaining discrepancy between theory and experiment.

We have considered the possibility that the inclusion of triple excitations in the MR-CC model[43] may be important. We have carried out calculations of the IPs of CH_2PH with two schemes, MR-CCSD + T(3) and MR-CCSD + T*(3), that partially include the essential effects of triple excitations in the MR-CC model.[43] The DZP basis set was used in these calculations, and the results are shown along with the original MR-CCSD DZP results in Table IX. Evidently, these effects are not important, at least for a DZP basis set.

Another potentially important factor in any comparison is the impossibility of a direct experimental determination of the vertical IP. Rather, experimental IPs are band maxima, which may differ by several tenths of an electronvolt from the true vertical IP.[48] When vibronic coupling is important a detailed vibronic calculation is necessary to obtain the correct vertical IP.[48,49] The difficulties of extracting experimental vertical IPs have also been remarked upon by von Niessen et al.[6b] In view of this, we believe that the errors in our best estimates of the IPs of CH_2PH may very well be slightly less than Table VII would indicate, but analysis of the

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(48) We thank a reviewer for reminding us of this point.

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vibrational structure and still more extensive calculations are needed to confirm this one way or the other.

Conclusions

We have seen that the QRHF-CC and MR-CC schemes are capable of calculating molecular IPs to a high accuracy. In deciding which method to use one must strike a balance between cost and accuracy. The QRHF-CCSD method, as presently implemented, requires separate CCSD calculations on the molecule and the lowest cationic states, although this is not necessary, as discussed below. The QRHF-CCSD method is reasonably accurate, although because it does not account for any effects of connected triple excitations, it may give poorer values for certain IPs than the QRHF-CCSDT-1 and MR-CC methods, as we have shown. Currently, the QRHF-CCSDT-1 method is also implemented by performing separate CCSDT-1 calculations on the molecule and cations of interest, and the iterative inclusion of triple excitations is 1 order of magnitude more expensive than a CCSD calculation.

For both QRHF-CCSD and QRHF-CCSDT-1 it is not necessary to do separate calculations, since in a slightly modified formulation the energy difference may be computed directly.[50] The direct calculation is, essentially, what would be done in the MR-CC scheme provided that a single determinant dominates the "model" function of the MR-CC procedure, which is usually the case.

The MR-CC method requires a CCSD calculation on the neutral molecule and then the determination of the amplitudes of those excitations which are not possible in the neutral molecule but which may occur in the cations (a much smaller number of amplitudes than in the initial CCSD calculation on the neutral molecule). Consequently, the total cost of an MR-CC calculation is less than that of two CC calculations. As we mentioned earlier, a single MR-CC calculation furnishes the whole set of IPs that may be obtained from the orbitals chosen to be active. It follows that the MR-CC method is the most economical of the three methods (and more economical than the HF-MBPT/CC methods), even if one wants only a single IP. The MR-CC method appears to be more accurate than the QRHF-CCSD method but not quite as accurate as the QRHF-CCSDT-1 approach, although except for the 5a′ IP of CH_2NH they give virtually identical results for the two molecules studied here. Extension of the MR-CC scheme to introduce "shake-up" effects requires consideration of additional sectors in the hierarchical Fock space approach.

We have reported valence IPs of methylenimine, methylenephosphine, and P_2. The results have been compared with data obtained from other theoretical techniques and experiment. In general, agreement is very good, showing that the new CC schemes are capable of a balanced treatment of the correlation energies of the neutral molecule and cations, suggesting that they should be valuable techniques for predicting and interpreting photoelectron spectra. Particular attention should be drawn to the MR-CC method, which is more economical than the other CC schemes, yet is almost as accurate as the separate state CCSDT-1 methods.

The work presented here represents a complete and accurate calculation of the principal valence IPs of methylenimine and methylenephosphine. Larger basis sets have been used than in previous work; highly accurate correlated methods have been employed; the 3a′ and 4a′ IPs of these molecules have been accurately calculated for the first time; and an accurate calculation of the separation of the lowest two cationic states of CH_2PH has been achieved. The experimental discrepancy of 0.1–0.3 eV should be further analyzed.

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Highly Asymmetric Electrolytes: A Comparison of Monte Carlo Simulations and the HNC Integral Equation

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Abstract: Computer simulation results are presented for a model electrolyte solution in which the ions are asymmetric in both charge and size. The asymmetry in size is 10:1, and in charge from 10:1 to 15:1. The ions are modeled in two different ways: (i) as charged hard spheres embedded in a dielectric continuum and (ii) using more realistic, "soft" potentials to model short-range interactions. In both cases the solvent is not present explicitly. The computer simulations are performed on a relatively large sample of particles and permit quantitative comparison with the integral equation approximations. Specifically, the accuracy of the hypernetted chain equation is examined. This approximate integral equation provides reasonable estimates for both the pair correlation functions and thermodynamic properties, even up to the region in which converged solutions disappear. However, systematic discrepancies with the simulation results are found as the charge asymmetry is increased. In brief, the hypernetted chain approximation places counterions too close to each other and also too close to the highly charged polyion. This leads to an underestimate of the polyion–polyion correlation and allows the polyions to come too close to each other. This affects the interpretation of intermicellar structure factors obtained by neutron scattering experiments. A second consequence is that the hypernetted chain approximation misplaces the region of phase separation.

1. Introduction

Polyelectrolytes, solutions of colloids, micelles, and globular proteins, which are a set of classical topics in physical chemistry and currently also popular areas of research, can be viewed as electrolytes asymmetric in both charge and size. Their properties in solution are dominated by the Coulombic interactions between the highly charged polyions and the small counterions. The mobility and activity of these counterions are reduced considerably below their values in a bulk simple electrolyte. When an external electric field is applied to such a solution, a fraction of the counterions is thought to move as an integral part of a polyion.

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