

**SLOW CONVERGENCE OF THE MØLLER-PLESSET PERTURBATION SERIES:
THE DISSOCIATION ENERGY OF HYDROGEN CYANIDE
AND THE ELECTRON AFFINITY OF THE CYANO RADICAL**

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Møller-Plesset perturbation expansions for hydrogen cyanide (HCN) and for cyanide anion (CN⁻) converge rapidly, whereas that for cyano radical (CN) converges only slowly. As a result, fourth-order Møller-Plesset theory leads to estimates of the dissociation energy of HCN and of the electron affinity of CN which are considerably overestimated. The results for cyano radical indicate that slow convergence of the UMP series in the case of strongly spin-contaminated wavefunctions can occur not only for stretched molecules but also for equilibrium structures.

1. Introduction

A widely used method of incorporating the effects of electron correlation into molecular-orbital calculations is Møller-Plesset perturbation theory [1,2]. Møller-Plesset methods have the important property of size consistency, giving additive results when applied to an assembly of isolated systems. This property is lacking in certain other correlation methods such as limited configuration interaction. Møller-Plesset methods are denoted by the order at which the perturbation series is truncated, calculations at second (MP2) [2], third (MP3) [2] and fourth (MP4) orders [3,4] now being considered routine.

For open-shell systems such as radicals, the Møller-Plesset expansion is based on molecular orbitals obtained with spin-unrestricted Hartree-Fock (UHF) theory, while for closed-shell species at equilibrium spin-restricted (RHF) orbitals are used. For closed-shell species away from equilibrium, either UHF or RHF orbitals may be used as the starting

point for the Møller-Plesset expansion. It is important to note that the UHF method leads to wavefunctions which are not eigenfunctions of the S^2 spin operator. Such wavefunctions will always be contaminated to some degree by electronic states of higher spin multiplicity.

Use of Møller-Plesset perturbation theory to calculate correlation energies is of practical value only if the perturbation series is rapidly convergent. Recent papers [5-7] have highlighted situations in which this is not the case. These involved molecules with geometries distorted far away from equilibrium. Knowles et al. [5] and Handy et al. [6] examined H₂O and NH₂ at geometries in which the bonds were stretched to 1.5 and 2 times the equilibrium values and found that the unrestricted Møller-Plesset (UMP) series was extremely slow to converge under such circumstances. Gill and Radom [7] found similar behaviour when examining the dissociation of the dihelium dication, He₂²⁺. In these papers, the very slow convergence of the UMP series was attributed to the presence of considerable spin contamination in the underlying UHF wavefunction.

It is interesting to ask if this slow UMP convergence is exhibited by any species *at equilibrium*. One

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class of molecules for which the UHF wavefunctions are known to be severely spin-contaminated is that of highly unsaturated radicals, such as cyano, CN^\cdot . It has recently been noted [8,9] that MP4 estimates of the electron affinity of this radical, i.e. the negative of the energy change for the reaction



are in poor agreement with experiment, even when large basis sets are used, and it has been suggested [8] that this may be a manifestation of slow UMP convergence for the radical. In the present paper, we examine the convergence behaviour of the Møller–Plesset series for the cyano radical, cyanide anion and hydrogen cyanide, and discuss the implications for calculations of the electron affinity of CN^\cdot and the dissociation energy of HCN.

2. Methods

Initial calculations were carried out using the GAUSSIAN 82 [10] system of programs and the configuration interaction program of Werner and Reinsch [11]. The basis set used, termed 6-311+G(d,p), consists of the standard split-valence plus polarization 6-311G(d,p) set [12] augmented with a set of diffuse s and p functions [13] on the heavy atoms. Spin-unrestricted theoretical methods employed include Hartree–Fock (UHF) theory, Møller–Plesset theory to second, third and fourth orders, coupled-cluster theory with double substitutions (CCD) [14], and configuration interaction with doubles (UCID) and with singles+doubles (UCISD). In addition, spin-restricted Hartree–Fock (RHF) and singles+doubles configuration interaction (RCISD) calculations were performed, with the RCISD calculations employing the first-order interacting space approximation [15]. The effect of quadruple excitations was accounted for in the CID and CISD calculations through use of the approximate formula due to Davidson [16], namely

$$\Delta E_Q \approx (1 - a_0^2) \Delta E_{\text{CI}} , \quad (2)$$

where a_0 is the coefficient of the Hartree–Fock determinant in the CID or CISD expansion and ΔE_{CI} is the correlation energy due to double or to single+double excitations.

In a second set of calculations, full configuration interaction was carried out using the program due to Handy and Knowles [17] and modified to yield Møller–Plesset energies to all orders [6]. The full CI calculations are only tractable with a small basis set, and the minimal STO-3G basis [18] was therefore used. Parallel calculations were performed for comparison purposes with the STO-3G basis set and each of the other methods noted above.

For all calculations, the UHF/6-31G(d) geometry of CN^\cdot ($r_{\text{CN}} = 1.1619 \text{ \AA}$) and the RHF/6-31G(d) geometries of CN^- ($r_{\text{CN}} = 1.1607 \text{ \AA}$) and HCN ($r_{\text{CN}} = 1.1325 \text{ \AA}$, $r_{\text{CH}} = 1.0591 \text{ \AA}$) were used. The carbon and nitrogen 1s orbitals were frozen in all of the post-Hartree–Fock calculations.

To enable comparison of theoretical and experimental reaction energies, the experimentally measured reaction enthalpies were corrected for thermal and zero-point vibrational energies. Such energies for HCN and CN^- were taken directly from ref. [19]. Following the procedure in this reference, the internal energies of CN^\cdot at 0 and 298 K were calculated using UHF/6-31G(d) vibrational frequencies scaled by a factor of 0.89.

3. Results and discussion

The dissociation energy (DE) of HCN is the energy change for the reaction



while the proton affinity (PA) of CN^- is given by the negative of the energy change for the reaction



The electron affinity (EA) of CN^\cdot has already been defined as the negative of the energy change in reaction (1). These three quantities, as calculated with the 6-311+G(d,p) basis set, are compared with the experimental values in table 1. It is convenient to discuss first the calculations of DE(HCN) and EA(CN^\cdot) followed by the calculations of PA(CN^-).

We note first that theoretical estimates of electron affinities are extremely dependent on the basis set used. With a basis such as 6-311+G(d,p), we would expect the calculated electron affinity to *underestimate* the experimental value by perhaps 30–60 kJ

Table 1

Total energies (in E_h), and the dissociation energy of HCN, electron affinity of CN^{\cdot} and proton affinity of CN^- (in kJ mol^{-1}), calculated with the 6-311+G(d,p) basis set

Method	Total energy			DE(HCN) ^{a)}	EA(CN^{\cdot})	PA(CN^-)
	HCN	CN^-	CN^{\cdot}			
RHF	-92.90138	-92.33493	-92.21097	500	325	1487
UHF	-92.90138 ^{b)}	-92.33493 ^{b)}	-92.22731	458	283	1487 ^{b)}
MP2	-93.19998	-92.63193	-92.46623	614	435	1491
MP3	-93.20021	-92.62889	-92.47223	599	411	1500
MP4DQ	-93.20302	-92.63205	-92.47501	599	412	1499
MP4SDQ	-93.20776	-92.63728	-92.48455	587	401	1498
MP4SDTQ	-93.22349	-92.65449	-92.49668	596	414	1494
CCD	-93.20346	-92.63192	-92.47642	597	408	1501
RCISD	-93.18545	-92.61372	-92.47988	540	351	1501
RCISD(Q) ^{c)}	-93.21146	-92.63993	-92.50862	533	345	1501
UCID	-93.18233 ^{b)}	-92.61042 ^{b)}	-92.46146	580	391	1502 ^{b)}
UCID(Q) ^{c)}	-93.20690 ^{b)}	-92.63499 ^{b)}	-92.48007	596	407	1502 ^{b)}
UCISD	-93.18545 ^{b)}	-92.61372 ^{b)}	-92.47486	553	365	1501 ^{b)}
UCISD(Q) ^{c)}	-93.21146 ^{b)}	-92.63993 ^{b)}	-92.50514	542	354	1501 ^{b)}
exp.				544 ± 20 ^{d)}	367 ± 3 ^{e)}	1486 ± 8 ^{f)}

^{a)} The energy of the hydrogen atom with this basis set is $-0.49981 E_h$.

^{b)} UHF and RHF are equivalent in this case.

^{c)} Incorporating Davidson correction for the effect of quadruple substitutions (see text).

^{d)} Derived from experimental heats of formation at 0 K [20] by correcting for zero-point vibrational energies.

^{e)} Derived from the experimental EA at 0 K [21] by correcting for zero-point vibrational energies.

^{f)} Derived from the experimental PA at 298 K as quoted in ref. [19] by correcting for thermal and zero-point vibrational energies.

mol^{-1} [8]. However, it can be seen from table 1 that the Møller-Plesset calculations of $EA(CN^{\cdot})$, as well as $DE(\text{HCN})$, lead to values substantially *greater* than experiment, the errors with the complete MP4 approach being 47 and 52 kJ mol^{-1} respectively. The coupled-cluster (CCD) method seems to suffer from the same problem as the Møller-Plesset calculations in these cases, the CCD values being close to those obtained at MP4DQ. The UCID method leads to only a small improvement and again leads to values greater than experiment. Introduction of single excitations into the unrestricted CI has a large effect, lowering $DE(\text{HCN})$ and $EA(CN^{\cdot})$ by 27 and 26 kJ mol^{-1} , respectively, leading finally to a UCISD(Q) value of $DE(\text{HCN})$ which is very close to experiment and of $EA(CN^{\cdot})$ which is 13 kJ mol^{-1} lower than the experimental value. The UCISD and UCISD(Q) results are also reasonably close to corresponding RCI values of $DE(\text{HCN})$ and $EA(CN^{\cdot})$. Note that the configuration interaction calculations for CN^{\cdot} based on *restricted* Hartree-Fock orbitals

lead to energies lower than those based on *unrestricted* orbitals; this is the first clue that the UHF wavefunction for CN^{\cdot} may be a poor starting point for subsequent correlation treatments.

Møller-Plesset and coupled-cluster calculations of $PA(CN^-)$ show none of the problems discussed above for $DE(\text{HCN})$ and $EA(CN^{\cdot})$. For example, even at the MP2 level, the calculated proton affinity (1491 kJ mol^{-1}) is close to the experimental value (1486 ± 8 kJ mol^{-1}). Higher orders of perturbation theory lead to similar agreement with experiment.

Why do the calculations of $DE(\text{HCN})$ and $EA(CN^{\cdot})$, on the one hand, and $PA(CN^-)$, on the other, show such widely differing errors relative to experiment? Examination of eqs. (1), (3) and (4) shows that the first two quantities both involve calculated energies for CN^{\cdot} , while the last involves only energies for HCN and CN^- . It would seem that the Møller-Plesset, UCID and CCD methods are behaving poorly in the case of the cyano radical.

In order to test this proposal, further calculations

were performed with the minimal STO-3G basis set. In such a basis set, the full CI result and Møller–Plesset energies to all orders may be obtained, thus enabling a critical examination of the convergence behaviour of the perturbation series. The results are shown in table 2. While the *absolute* values of

DE(HCN), EA(CN[·]) and PA(CN⁻) are of course very poor in such a small basis set, the *trends* in these calculations seem to follow closely those observed with the larger basis.

It is clear from table 2 that the Møller–Plesset series for CN⁻ and for HCN both converge rapidly, the

Table 2

Total energies (in E_h), and the dissociation energy of HCN, electron affinity of CN[·] and proton affinity of CN⁻ (in kJ mol⁻¹), calculated with the STO-3G basis set

Method	Total energy			DE(HCN) ^{a)}	EA(CN [·])	PA(CN ⁻)
	HCN	CN ⁻	CN [·]			
RHF	-91.67377	-90.93766	-90.99752	550	-157	1933
UHF	-91.67377 ^{b)}	-90.93766 ^{b)}	-91.01943	493	-214	1933 ^{b)}
MP2	-91.82033	-91.07143	-91.11411	629	-112	1966
MP3	-91.82242	-91.06862	-91.12203	614	-140	1979
MP4DQ	-91.82679	-91.07065	-91.12599	615	-145	1985
MP4SDQ	-91.82719	-91.07254	-91.13358	596	-160	1981
MP4SDTQ	-91.82846	-91.07603	-91.13538	595	-156	1976
MP5	-91.83129	-91.07539	-91.14221	584	-175	1985
MP6	-91.83233	-91.07694	-91.14855	570	-188	1983
MP7	-91.83264	-91.07678	-91.15276	560	-199	1985
MP8	-91.83289	-91.07699	-91.15666	551	-209	1985
MP9	-91.83304	-91.07703	-91.15940	544	-216	1985
MP10	-91.83314	-91.07704	-91.16183	538	-223	1985
MP11	-91.83313	-91.07704	-91.16362	533	-227	1985
MP12	-91.83317	-91.07706	-91.16515	529	-231	1985
MP13	-91.83315	-91.07705	-91.16631	526	-234	1985
MP14	-91.83318	-91.07706	-91.16727	523	-237	1985
MP15	-91.83316	-91.07706	-91.16800	521	-239	1985
MP16	-91.83318	-91.07706	-91.16859	520	-240	1985
MP17	-91.83316	-91.07706	-91.16904	519	-241	1985
MP18	-91.83318	-91.07706	-91.16939	518	-242	1985
MP19	-91.83316	-91.07706	-91.16965	517	-243	1985
MP20	-91.83318	-91.07706	-91.16985	517	-244	1985
MP21	-91.83316	-91.07706	-91.16999	516	-244	1985
MP22	-91.83318	-91.07706	-91.17010	516	-244	1985
MP23	-91.83317	-91.07706	-91.17017	516	-244	1985
MP24	-91.83317	-91.07706	-91.17021	516	-245	1985
CCD	-91.82980	-91.07187	-91.13124	609	-156	1990
RCISD	-91.82027	-91.06622	-91.15245	528	-226	1980
RCISD(Q) ^{c)}	-91.83135	-91.07467	-91.16983	512	-250	1987
UCID	-91.81999 ^{b)}	-91.06494 ^{b)}	-91.12506	600	-158	1982 ^{b)}
UCID(Q) ^{c)}	-91.83094 ^{b)}	-91.07300 ^{b)}	-91.13228	609	-156	1990 ^{b)}
UCISD	-91.82027 ^{b)}	-91.06622 ^{b)}	-91.14830	539	-216	1980 ^{b)}
UCISD(Q) ^{c)}	-91.83135 ^{b)}	-91.07467 ^{b)}	-91.16992	512	-250	1987 ^{b)}
full CI	-91.83317	-91.07706	-91.17006	516	-244	1985

^{a)} The energy of the hydrogen atom with this basis set is $-0.46658 E_h$.

^{b)} UHF and RHF are equivalent in this case.

^{c)} Incorporating Davidson correction for the effect of quadruple substitutions (see text).

fourth-order total energies being within 1 and 5 mE_h , respectively, of the full CI result. However, this is not the case for CN^+ , the UMP4 energy for this species being 35 mE_h higher than the full CI result. The convergence of the UMP series is indeed slow; one would require an 18th-order calculation to obtain an energy within 1 mE_h of the correct result! The consequence is that Møller–Plesset calculations of DE(HCN) and EA(CN^+), both of which involve the energy of CN^+ , are also very slow to converge.

The poor convergence of the UMP series for CN^+ is no doubt linked to the high degree of spin contamination in the UHF wavefunction for this species (the expectation value of S^2 being 1.13 with the 6-311+G(d,p) basis set and 1.23 with STO-3G). The large difference between the UCID and UCISD energies for CN^+ , together with the poor performance of the CCD method for this species, indicates that single substitutions are extremely important in improving the UHF wavefunction. Single substitutions only enter the Møller–Plesset series at fourth order, and then only through interaction with the double substitutions. It would seem that, if a UHF starting point is to be used, correlation methods which account well for the effects of single excitations are needed in order to obtain reliable estimates of the energy of the cyano radical.

4. Conclusions

The following conclusions emerge from this study:

(i) The Møller–Plesset perturbation series converges rapidly for HCN and CN^- but only slowly for CN^+ . Consequently, truncating the series at low orders leads to values of DE(HCN) and EA(CN^+) which are considerably overestimated.

(ii) The coupled-cluster doubles (CCD) and configuration interaction doubles (UCID) methods based on UHF orbitals also perform poorly in the case of CN^+ whereas the UCISD method yields better results. This indicates that single excitations are very important in improving the severely contaminated UHF wavefunction for this radical.

(iii) It would seem that, for systems in which the UHF wavefunction contains considerable spin contamination, correlation methods better than MP4 or CCD need to be used in order to obtain reliable energies.

(iv) The present results indicate that the slow convergence of the UMP series in the case of strongly spin-contaminated wavefunctions can occur not only for stretched molecules but also for equilibrium structures.

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References

- [1] C. Møller and M.S. Plesset, *Phys. Rev.* 46 (1934) 618.
- [2] J.A. Pople, J.S. Binkley and R. Seeger, *Intern. J. Quantum Chem. Symp.* 10 (1976) 1, and references therein.
- [3] J.A. Pople, R. Krishnan, H.B. Schlegel and J.S. Binkley, *Intern. J. Quantum Chem.* 14 (1978) 545.
- [4] R. Krishnan, M.J. Frisch and J.A. Pople, *J. Chem. Phys.* 72 (1980) 4244.
- [5] P.J. Knowles, K. Somasundram, N.C. Handy and K. Hirao, *Chem. Phys. Letters* 113 (1985) 8.
- [6] N.C. Handy, P.J. Knowles and K. Somasundram, *Theoret. Chim. Acta* 68 (1985) 87.
- [7] P.M.W. Gill and L. Radom, *Chem. Phys. Letters* 132 (1986) 16.
- [8] J. Baker, R.H. Nobes and L. Radom, *J. Comput. Chem.* 7 (1986) 349.
- [9] J.V. Ortiz, *J. Chem. Phys.* 86 (1987) 308.
- [10] J.S. Binkley, M.J. Frisch, D.J. DeFrees, K. Raghavachari, R.A. Whiteside, H.B. Schlegel, E.M. Fluder and J.A. Pople, GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, PA 15213, USA.
- [11] H.-J. Werner and E.-A. Reinsch, *J. Chem. Phys.* 76 (1982) 3144.
- [12] R. Krishnan, J.S. Binkley, R. Seeger and J.A. Pople, *J. Chem. Phys.* 72 (1980) 650.
- [13] T. Clark, J. Chandrasekhar, G.W. Spitznagel and P. von R. Schleyer, *J. Comput. Chem.* 4 (1983) 294.
- [14] K. Raghavachari, *J. Chem. Phys.* 82 (1985) 4607, and references therein.
- [15] A.D. McLean and B. Liu, *J. Chem. Phys.* 58 (1973) 1066.
- [16] E.R. Davidson, in: *The world of quantum chemistry*, ed. R. Daudel (Reidel, Dordrecht, 1974) pp. 17–30.
- [17] P.J. Knowles and N.C. Handy, *Chem. Phys. Letters* 111 (1984) 315.
- [18] W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Chem. Phys.* 51 (1969) 2657.
- [19] D.J. DeFrees and A.D. McLean, *J. Comput. Chem.* 7 (1986) 321.
- [20] JANAF thermochemical tables (Natl. Bur. Std., Washington, 1971).
- [21] J. Berkowitz, W.A. Chupka and T.A. Walker, *J. Chem. Phys.* 50 (1969) 1497.