# Correlation Contribution to Ionization Potentials and Excitation Energies of Ammonia, Nitrogen, Oxygen, and Ethylene

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**Abstract:** The total and effective molecular pair correlation energies have been computed for ammonia, nitrogen, oxygen, and ethylene molecules at their neutral and positively ionized states. The total correlation energies are partitioned into $\sigma$, $\sigma$–$\pi$, and $\pi$ parts whenever it is possible. The correlation contributions to the barrier energy, ionization potential, and excitation energies are also calculated. The correlation contributions to the ionization potentials are found to be 11–14% of the experimental values. HF limits of the energies are predicted for the cations by using the calculated correlation energies.

Chemically interesting quantities, such as binding energies, ionization potentials, etc., are small differences between comparably large energy values. Therefore, even very small errors in calculating the total energies might be reflected as significant contributions to these quantities. The extensive study of the ground state correlation contribution to the binding energies is, in general, 23–35% of the experimental values.[1] The detailed analysis of the correlation effects in the neutral and ionized states of acetylene has also revealed that there is a considerable contribution of the correlation to the ionization potential and excitation energies and that the semiempirical approach gives more reliable results than the limited configuration interaction calculations.[2,3]

Since the exact energy of any state may be assumed to be the sum of the Hartree–Fock (HF), correlation (CORR), and relativistic (R) energies, the energy difference between two states can be written as

$$\Delta E = \Delta E_{\mathrm{HF}} + \Delta E_{\mathrm{CORR}} + \Delta E_{\mathrm{R}} \qquad (1)$$

When we are dealing with ionization potentials, $\Delta E$'s will be replaced by more familiar notation IP.

Generally, the relativistic effects are assumed to be coming mainly from the core electrons. Therefore, its contribution is neglected in the processes involving higher level electrons. This seems rather reasonable when there is no change in the number of electrons. Although it may cause error upon ionization, we still neglect it in the present calculations.

The correlation energy of a molecule is defined as the difference between the exact nonrelativistic energy and the HF energy.[4] Since this definition is based on two quantities neither of which can be known exactly, the correlation energy can only be estimated. If the relativistic energy were known, the exact nonrelativistic energy could be obtained from the experimental energy, and if the true HF limit has been reached, by taking the difference, the so-called "experimental" correlation energy could be found. However, the relativistic effects for molecules are not known precisely to allow us to make reliable estimates of true nonrelativistic energies and the HF limit has not been reached yet for the molecular ions. Therefore, a method independent of HF calculations must be used to estimate the correlation energy.

## The Method

For estimating the molecular correlation energies, the semiempirical "Effective Pair Correlation Energy" method with the "F2$\sigma$" approximation[5] is used. This method is referred to as the EPCE-F2$\sigma$ method. The previous applications of this method have indicated that the correlation energies of molecules can be estimated with less than a 5% error range and that the results are independent of HF calculations and not strongly dependent on the choice of the basis set.[1-3,5-7]

In the EPCE-F2$\sigma$ method, the total correlation energy is approximated as the sum of the effective molecular pair correlation energies. The effective molecular pair correlation energies, in turn, are given in terms of the effective atomic pair correlation energies, the numbers of the electrons occupying the molecular orbitals, and the partial gross atomic populations. For details of the method and its parametrization the reader is referred to ref 5.

The effective pair correlation energies are made of all-external, semi-internal, and internal correlation parts. The latter two parts are strongly dependent on the electron distribution. The EPCE-F2$\sigma$ method, recently, has been applied to the localized molecular orbitals and their transferabilities have been discussed in detail.[7] However, in the case of ionization or excitation processes we have to use delocalized canonical orbitals.

The partial gross atomic populations are obtained from the self-consistent field (SCF) wave functions taken from the literature.[8-11]

## $\sigma$, $\sigma$–$\pi$, $\pi$ and Pair Correlation Energies

The effective molecular pair correlation energies and their sums for ammonia are given in Table I. Since $\bar{\epsilon}_{kl} = \bar{\epsilon}_{lk}$, only those pairs satisfying the $k \leq l$ relation are listed. The $\sigma$, $\sigma$–$\pi$, $\pi$, and total correlation energies of oxygen, nitrogen, and ethylene are given in Table II. To simplify the entries in these tables, the following notation has been used: PyrA = pyramidal ammonia whose wave functions are taken from ref 8; PyrBP, PIB, and PIBP = pyramidal ammonia's positive ion, planar ammonia, and planar ammonia's positive ion, respectively. The wave functions for these are taken from ref 9; X, A, B, C, XP, and BP = X $^1\Sigma_g{}^+$, A $^3\Sigma_u{}^+$, B $^3\Pi_g$, C $^3\Pi_u$ states of nitrogen, and X $^2\Sigma_g{}^+$ and B $^2\Sigma_u{}^+$ states of nitrogen positive ion, respectively; OX, Oa, and OXP = X $^3\Sigma_g$ and a $^1\Delta_g$ states of oxygen, and X $^2\Pi_g$ state of oxygen positive ion, respectively. The wave functions for all states of $N_2$, $N_2{}^+$, $O_2$, and $O_2{}^+$ are taken from ref 10.

From the investigation of the pair correlation energies, the following conclusions have been drawn;

1. Intra- and inter-orbital pair correlation energies among $1\sigma$ and $1\sigma$-other orbital interactions do not change considerably upon the change of the state or upon ionization. Therefore, they may be assumed as transferable. This has been discussed in ref 7.

2. The pair correlation energies among the valence orbitals generally increase, in absolute value, upon ionization. This is due to the dependence of internal and semi-internal contri-

**Table I.** Pair Correlation Energies in the Ground and Postively Ionized States of the Pyramidal and Planar Ammonia[a]

| Pairs | PyrA | PyrB | PyrBP | PlB | PlBP |
|---|---|---|---|---|---|
| $1\sigma$–$1\sigma$ | −1.246 | −1.247 | −1.246 | −1.246 | −1.246 |
| $2\sigma$ | −0.059 | −0.058 | −0.063 | −0.057 | −0.063 |
| $3\sigma$ | −0.060 | −0.060 | −0.072 | −0.060 | −0.072 |
| $4\sigma$ | −0.060 | −0.060 | −0.072 | −0.060 | −0.072 |
| $5\sigma$ | −0.098 | −0.097 | −0.100 | −0.104 | −0.105 |
| $2\sigma$–$2\sigma$ | −0.367 | −0.346 | −0.379 | −0.318 | −0.352 |
| $3\sigma$ | −0.505 | −0.485 | −0.540 | −0.471 | −0.543 |
| $4\sigma$ | −0.505 | −0.485 | −0.540 | −0.471 | −0.543 |
| $5\sigma$ | −0.488 | −0.486 | −0.551 | −0.455 | −0.559 |
| $3\sigma$–$3\sigma$ | −0.600 | −0.574 | −0.605 | −0.594 | −0.622 |
| $4\sigma$ | −0.375 | −0.371 | −0.420 | −0.369 | −0.420 |
| $5\sigma$ | −0.441 | −0.437 | −0.497 | −0.394 | −0.462 |
| $4\sigma$–$4\sigma$ | −0.600 | −0.574 | −0.605 | −0.594 | −0.622 |
| $5\sigma$ | −0.441 | −0.437 | −0.497 | −0.394 | −0.462 |
| $5\sigma$–$5\sigma$ | −0.704 | −0.703 |  | −0.781 |  |
| Total | −9.581 | −9.400 | −7.894 | −9.204 | −7.853 |

[a] All values are in eV. See text for the notation.

**Table II.** $\sigma$, $\sigma$–$\pi$, $\pi$, and Total Correlation Energies of Nitrogen, Oxygen, and Ethylene Molecules[a]

| Molecule, state | $E^{\sigma}{}_{\mathrm{CORR}}$ | $E^{\sigma-\pi}{}_{\mathrm{CORR}}$ | $E^{\pi}{}_{\mathrm{CORR}}$ | Total |
|---|---|---|---|---|
| $N_2$, X | −7.442 | −5.184 | −2.256 | −14.882 |
| A | −7.563 | −5.224 | −1.736 | −14.523 |
| B | −5.682 | −5.384 | −3.384 | −14.450 |
| C | −5.815 | −5.156 | −3.384 | −14.355 |
| XP | −6.134 | −4.620 | −2.256 | −13.010 |
| BP | −6.145 | −4.418 | −2.256 | −12.819 |
| $O_2$, OX | −6.288 | −6.810 | −3.690 | −16.788 |
| Oa | −6.289 | −6.792 | −4.260 | −17.341 |
| OXP | −6.696 | −6.055 | −2.710 | −15.468 |
| $C_2H_4$, neutral | −11.663 | −2.844 | −0.849 | −15.356 |
| cation | −12.598 | −1.553 |  | −14.151 |

[a] All values are in eV. See the text for the notation.

**Table III.** Ionization Potentials (in eV)

| Molecule, states |  | $IP_{\mathrm{CORR}}$ | $IP_{\mathrm{cal}}$ | $IP_{\mathrm{K}}$ | $IP_{\mathrm{obsd}}$ |
|---|---|---|---|---|---|
| $NH_3$, | PyrBP–PyrB | 1.706 | 9.50 | 10.03 |  |
|  | PlBP–PlB | 1.351 | 8.22 | 8.91 |  |
|  | PlBP–PyrB | 1.547 | 8.87 | 8.91 | 10.6 ± 0.5[a] |
| $N_2$, | XP–X | 1.872 | 16.67 | 14.81 | 15.576[b] |
|  | BP–B | 1.631 | 21.51 | 19.87 | 18.72[b] |
| $O_2$, | OXP–OX | 1.320 | 12.14 | 10.80 | 12.2[b] |
| $C_2H_4$ |  | 1.205 | 10.39 | 10.04 | 10.5[c] |

[a] See ref 15. [b] From ref 10. [c] From ref 16.

**Table IV.** Excitation Energies (in eV)

| Molecule, state | $\Delta E_{\mathrm{CORR}}$ | $\Delta E_{\mathrm{cal}}$ | $\Delta E_{\mathrm{obsd}}$[a] |
|---|---|---|---|
| $N_2$, A–X | 0.359 | 7.55 | 7.70 |
| B–X | 0.432 | 7.92 | 8.12 |
| C–X | 0.527 | 13.28 | 11.25 |
| $N_2^+$, BP–XP | 0.191 | 5.26 |  |
| $O_2$, Oa–OX | −0.553 | 1.67 | 1.00 |

[a] From ref 10.

butions on the 2p electron populations of the constituent atoms.

3. There has been no change observed for the same $\pi$–$\pi$ type pairs upon ionization or change of state. This is due to the original assumption in the EPCE-F2$\sigma$ method which neglects the semi-internal and internal contributions coming from $\pi$–$\pi$ interactions.

There have been two different calculations carried out for the ground state of pyramidal ammonia to reinvestigate the dependence of the results on the choice of the wave functions. The difference between the total correlation energies, obtained by using the wave functions taken from ref 8 and 9, is only 0.18 eV. In general the valence pair correlation energies in PyrA are greater, in absolute value, than PyrB. Since Kaldor and Shavitt[9] give the wave functions for both neutral and cation states, PyrB results are used when obtaining the correlation contribution to the barrier energy and ionization potential.

If there is a $\pi$ electron ionization, such as in $O_2$ or $C_2H_4$, the $\sigma$ part of the correlation increases in absolute value although there is a decrease in $\sigma$–$\pi$ and $\pi$ parts.

## Correlation Contribution to the Molecular Properties

If the pair correlation energies were totally transferable the sum of the pair correlation energies between the ionizing electron and others would yield the correlation contribution to the ionization potential. Due to the increase in absolute value of almost all valence electron pair correlation energies, this sum can only be an upper limit.[6]

Since the HF energies for most of the excited or ionized states are not known precisely, the HF contribution to the energy difference in eq 1 can be thought of as the SCF contribution, $\Delta E_{\mathrm{SCF}}$, and the error in this is $\Delta^2 E_{\mathrm{SCF}}$. If the errors in the SCF calculations for two states are comparable, the energy difference can be estimated using only simple SCF and correlation energy calculations.

The correlation contribution to the barrier energy of $NH_3$ is found to be 0.196 eV. This value seems better than 0.27 ± 0.06 obtained for the localized orbitals[7] and comparable to 0.160 eV obtained by Bender[12] and experimental values 0.250 and 0.209 eV reported by Bender[12] and by Lehn,[13] respectively.

The ionization potentials and the correlation contributions to them are given in Table III. $IP_{\mathrm{cal}}$ is the sum of the SCF and correlation contributions. $IP_{\mathrm{K}}$ is obtained by Koopmans' theorem.[14] With the exception of the $N_2$, the SCF values are improved after the addition of the correlation contribution. Although the Koopmans' theorem yields better results for $NH_3$, in the case of $O_2$ and $C_2H_4$ there is good agreement with the experimental values.

The correlation contribution and calculated and observed values for excitation energies are given in Table IV. With the exception of the C $^3\Pi_u$–X $^1\Sigma_g$ transition of nitrogen, all SCF values are improved with the addition of the correlation contributions.

The HF limit of the energy for a given cation can be predicted by using the HF energy of the molecular ground state, the experimental ionization potential, and the estimated correlation correction to it.

$$E^{+}{}_{\mathrm{HF}}(\text{predicted}) = E^{g}{}_{\mathrm{HF}} + \mathrm{IP}_{\mathrm{exp}} - \mathrm{IP}_{\mathrm{CORR}} \qquad (2)$$

This predicted value may be used as a criterian in the real HF calculations for this particular ion.

If −1529.93 eV for pyramidal ammonia given by Rajagopal,[16] −2965.77 eV for X $^1\Sigma_g^+$ state of $N_2$ given by Cade et al.,[17] −4072.36 eV for the X $^3\Sigma_g^-$ state of $O_2$ given by Schaefer,[18] and −2122.81 eV for $C_2H_4$ given by Dunning et al.[19] are used as HF energies of the ground states, −1520.98 eV for planar $NH_3^+$, −2951.06 eV for the X $^2\Sigma_g^+$ state of $N_2^+$, −4061.48 eV for the X $^2\Pi_g$ state of $O_2^+$, and −2113.52 eV for $C_2H_4^+$ are predicted as the HF energy limits. The limit predicted for $N_2^+$ is comparable to the ab initio result, −2949.78 eV, reported by Cade et al.[17]

## Conclusion

The effective molecular pair correlation energies between valence electrons are found to change considerably upon ionization due to the nontransferable, correlation effects. The relative contribution to the ionization potential is higher for the electron pairs in the higher level orbitals. The total correlation contribution to the ionization potential for the investigated systems is found to be 11–14% of the experimental IP.

Rather good agreements have been observed, for some systems, between the calculated and experimental ionization potentials although SCF errors are not included.

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## References and Notes

(1) O. Sinanoğlu and H. Ö. Pamuk, *J. Am. Chem. Soc.*, **95**, 5435 (1973).
(2) A. J. Duben, L. Goodman, H. Ö. Pamuk, and O. Sinanoğlu, *Theor. Chim. Acta*, **30**, 177 (1973).
(3) H. Ö. Pamuk, *Middle East Tech. Univ. J. Pure Appl. Sci.*, **6**, 231 (1973).
(4) P. O. Löwdin, *Adv. Chem. Phys.*, **2**, 207 (1959).
(5) H. Ö. Pamuk, *Theor. Chim. Acta*, **28**, 85 (1972).
(6) H. Ö. Pamuk, *Middle East Tech. Univ. J. Pure Appl. Sci.*, **4**, 103 (1971).
(7) H. Ö. Pamuk, *Theor. Chim. Acta*, to be published.
(8) W. A. Palke and W. N. Lispcomb, *J. Am. Chem. Soc.*, **88**, 2384 (1966).
(9) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **45**, 888 (1966).
(10) R. C. Sahni and E. J. De Lorenzo, *J. Chem. Phys.*, **42**, 3612 (1965).
(11) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968).
(12) C. F. Bender, *Theor. Chim. Acta*, **16**, 401 (1970).
(13) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 331 (1970).
(14) T. A. Koopmans, *Physica (Utrecht)*, **1**, 104 (1933).
(15) Experimental values are in between 10.1 and 11.2 eV. See: R. W. Kiser, "Tables of Ionization Potentials", TID-6142, Kansas State University, Manhattan, Kansas, 1960.
(16) P. Rajagopal, *Z. Naturforsch., A*, **20**, 1557 (1965).
(17) P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.*, **44**, 1973 (1966).
(18) H. F. Schaefer III, "The Electronic Structure of Atoms and Molecules", Addison-Wesley, Reading, Mass., 1972, p 215.
(19) T. H. Dunning, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, **4**, 147 (1969).

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# Free Energies and Free Energies of Activation for Ion Pairing and Hydrogen Bonding to an Anion Radical

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**Abstract:** The equilibria and rates were determined for two processes: (1) hydrogen bonding of *p*-cyanonitrobenzene radical anion by methanol in hexamethylphosphoramide (HMPA) and (2) ion pairing of this anion radical with $K^+$ in the same solvent. It was found that $\Delta G°$ for the formation of the ion paired species is smaller than that for the formation of the hydrogen bonded species. However, the formation of the hydrogen bond results in a larger perturbation of the electronic structure of the anion radical. This is probably due to the fact that the hydrogen bonding proton can approach the $NO_2$ group of the anion radical more closely than can the solvated cation. The rate of ion pair formation ($k_{\mathrm{If}} = 4.6 \times 10^8$ $M^{-1}$ $s^{-1}$) is large and probably encounter controlled, while that of hydrogen bond formation to the anion radical is about 60 times slower ($k_{\mathrm{Hf}} = 7.5 \times 10^6$ $M^{-1}$ $s^{-1}$). The free energy of activation necessary to break the hydrogen bond to the anion radical is 0.4 kcal/mol less than that necessary to break up the ion pair complex.

It is well recognized that two of the most important phenomena in the determination of solvation energies of anions are hydrogen bonding between solvent and anion and ion pairing. Consequently, there have been a large number of reports concerning the thermodynamic parameters controlling ion pair formation in a wide variety of solvent anion systems. Furthermore, these studies have been carried out using a wide variety of instrumental techniques.[1] Hydrogen bonding, on the other hand, is just as important in protic solvents in controlling the thermodynamic stability of anions, but there are few reports of thermodynamic parameters controlling hydrogen bonding to anions. This is true because of the experimental difficulties and complexities that arise from competing interactions such as ion pairing and solvent–solvent interactions. These problems are discussed in a recent report on the thermodynamic parameters controlling hydrogen bonding to the $Cl^-$ ion in solution by Benoit and co-workers.[2] The enthalpies and free energies of hydrogen bond formation to the $Cl^-$ ion reported by these workers must really represent reactions that are much more complex than that shown in eq 1. Since HR is

$$\begin{aligned}&Cl^-(\text{solution}) + HR(\text{solution})\\ &\qquad\qquad \rightleftarrows Cl^- \cdots HR(\text{solution}) \qquad (1)\end{aligned}$$

a secondary solvent, there are interactions between HR and the solvent. Also, the counterion is possibly involved. This interesting work of Benoit and co-workers involves the use of NMR, calorimetry, vapor pressure measurements, and solubility measurements.

Electron spin resonance (ESR) has also been recently used to obtain the free energies of the hydrogen bond exchange reaction (where the hydrogen bond is exchanged between the primary solvent and an anion radical) in hexamethylphosphoramide (HMPA) (see eq 2).[3] In HMPA ion pairing is not

$$X\cdot^- + HMPA \cdots HR \rightleftarrows X\cdot^- \cdots HR + HMPA \qquad (2)$$

a complication.[4] Furthermore, the free energy and enthalpy of hydrogen bonding to the solvent can be determined via NMR measurements and subtracted out to yield the actual free energies of hydrogen bonding to the anion radical.[3,5,6]

Even though there are many reports on the thermodynamic parameters controlling ion pairing and a few reports on these parameters for hydrogen bonding to anions,[7] the literature is devoid of reports on the kinetics of hydrogen bond formation to anions, and there is only one report to our knowledge on the rate constant for ion pair formation from the free ions.[8] It was our intention to measure the rate constants for formation and