Theoret. Chim. Acta (Berl.) 38, 303—309 (1975)

# Application of the Independent Electron Pair Approach to the Calculation of Excitation Energies, Ionization Potentials, and Electron Affinities of First Row Atoms

Volker Staemmler
Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Germany

Martin Jungen
Physikalisch-chemisches Institut, Universität Basel, Klingelbergstr. 80, CH-4056 Basel, Switzerland

Received July 29, 1974/April 4, 1975

Excitation energies, first ionization potentials and electron affinities of first row atoms are calculated with a spin-adapted independent electron pair approximation (IEPA) combined with the direct determination of pair natural orbitals (PNOs). To enable comparison with molecular calculations Gaussian basis sets are used which are small enough to be also applicable to molecules. IEPA results for the above mentioned properties are accurate to 0.1–0.3 eV which is almost one order of magnitude better than the corresponding SCF-results. The same accuracy can be expected for molecules in which a localization of the doubly and singly occupied orbitals is possible, for instance for small hydrides. This is supported by the results of calculations on carbon hydrides.

*Key words:* Independent electron pair approach – First row atoms, excitation energies of ~

## 1. Introduction

The "independent electron pair approximation" (IEPA) combined with the direct calculation of "pair natural orbitals" (PNO's) [1, 2] may be regarded as a good first step beyond the Hartree-Fock model in order to account for electron correlation in atoms and molecules [3–7]. It has been described explicitly [2, 8, 9] and applied successfully [2, 6–10 and references therein] to a large number of closed shell states as well as to some open shell systems [3–5, 11–13]. Recently, various schemes have been discussed [3–7, 9, 14] which try to overcome the shortcomings of IEPA in slightly different ways.

In the last years we have published a series of calculations on open-shell first row hydrides ($BH_2$ [11], small carbenes [12, 13], $CH_3$ [15]) performed with our spin-adapted IEPA-PNO-program for simple open shell states as described in Ref. [16]. We claimed our IEPA results for excitation energies, electron affinities etc. to be in error by not more than 0.1–0.3 eV which is almost one order of magnitude more reliable than the corresponding SCF-results.

To support this conclusion we present in this paper applications to excitation energies, ionization potentials and electron affinities of first row atoms. These calculations are performed with basis sets of the same size as in our molecular calculations in order to give a meaningful comparison and will not compete in accuracy with the large number of very accurate atomic calculations using large scale CI methods [17] or the symmetry-adapted IEPA-scheme [18–23].

In comparing atomic and molecular IEPA calculations some difficulties arise since the IEPA results are not invariant under unitary transformations of the occupied SCF-orbitals. Whereas this is not very serious for atoms [19], it can cause rather large errors for molecules [6, 7, 24–26]. The choice of localized SCF-orbitals leads to the most reliable IEPA results, since the interaction terms between the individual pairs are minimal [6, 7]. But generally for open shell molecular states a complete localization is not possible. Thus, our conclusions hold only for hydrides and related systems where the singly occupied canonical orbitals are already localized on the heavy atom and a localization of the doubly occupied orbitals can be performed separately.

## 2. Valence Shell Correlation Energies of the Ground States of First Row Atoms

Our spin-adapted open-shell IEPA-PNO program is a straightforward extension of the corresponding closed shell program used by Jungen and Ahlrichs [2]; a detailed description is given elsewhere [16]. To enable the comparison of our results with Nesbet's "atomic Bethe-Goldstone" calculations [22, 23, 27–29] we have to mention that the contributions of the singly substituted configurations are included in the "semi-internal pair excitations" [30, 31] and need not to be calculated separately. This is a consequence of the use of spin- adapted configurations since singly and doubly substituted configurations are mixed in the process of projecting out the correct spin function [16, 32].

The starting point for the IEPA calculation of correlation energies is a restricted HF-wavefunction. Since we did not impose the restriction that doubly and singly occupied orbitals must have the same radial part, we get for some states (e.g. O and F ground states) spatially unrestricted SCF-wavefunctions. This affects the SCF- and IEPA-energies only slightly, but leads to different orbital energies for doubly and singly occupied $p$-orbitals (see Section 3).

The basis used for our atomic calculations consisted of contracted Gaussian lobe functions. The standard basis was a $10s, 5p$ Huzinaga set [33] with (4, 2, 1, 1, 1, 1) and (2, 1, 1, 1) contraction to $6s$ and $4p$ groups. For the calculation of valence shell correlation energies we augmented this basis by two $d$ sets (each of them containing 5 components) with exponents similar to those optimized in [7] for first row hydrides. For negative ions and for excited states involving $3s$-AO's [e.g. in O($^5S_u$), F($^4P_g$), Ne($^3P_u$)] some more diffuse basis functions are necessary: We took one further $s, p$ set with an exponent of about 1/3 of the smallest exponent in the standard set for negative ions and three $s$ lobes with reasonably decreasing exponents in order to describe the $3s$-AO's.

Table 1 contains our SCF- and valence shell IEPA correlation energies $E^V_{\mathrm{IEPA}}$ for the ground states of the atoms Be to Ne, compared to Clementi's near Hartree-Fock SCF energies [34] and to Nesbet's [29] values of valence shell correlation energies. For O, F, and Ne we started both from canonical and localized orbitals,

Table 1. IEPA valence shell correlation energies of the ground states of first row atoms (all energies in a.u.)

| Atom | State | $E_{\mathrm{SCF}}$ | $E^V_{\mathrm{IEPA}}$ | $N_pN_d$[a] | $E_{\mathrm{SCF}}$ [34] | $E^V_{\mathrm{corr}}$ [29][c] |
|---|---|---|---|---|---|---|
| Be | $^1S_g$ | −14.57249 | −0.04477 | 1 1 | −14.57302 | −0.04535 |
| B | $^2P_u$ | −24.52748 | −0.06809 | 3 3 | −24.52902 | −0.07239 |
| C | $^3P_g$ | −37.68418 | −0.09293 | 6 4 | −37.68861 | −0.10011 |
| N | $^4S_u$ | −54.39309 | −0.11468 | 10 4 | −54.40091 | −0.12998 |
| O | $^3P_g$ | −74.79737 | −0.16568 | 13 9 | −74.80936 | −0.19107 |
| | | | −0.16901 | 13 6[b] | | |
| F | $^2P_u$ | −99.39047 | −0.22109 | 15 10 | −99.40932 | −0.25337 |
| | | | −0.22265 | 15 5[b] | | |
| Ne | $^1S_g$ | −128.51686 | −0.28110 | 16 6 | −128.54701 | −0.31727 |
| | | | −0.27544 | 16 3[b] | | |

[a] $N_p$ number of spin-adapted valence shell pairs.
$N_d$ number of non-equivalent valence shell pairs.

[b] IEPA calculation starting from localized orbitals.

[c] Contributions of singly substituted configurations of L-shell orbitals included.

but the differences in $E^V_{\mathrm{IEPA}}$ are quite small. This has been observed previously for atoms [7, 19, 24–26], but does not generally hold for molecules. The absolute errors of our results – both for $E_{\mathrm{SCF}}$ and $E^V_{\mathrm{IEPA}}$ – increase quite rapidly from Be to Ne, both being in the order of 0.0005 a.u. for Be and 0.035 a.u. for Ne. For $E_{\mathrm{SCF}}$ this is due to the deficiencies of our $s, p$ basis, for $E^V_{\mathrm{IEPA}}$ also the lack of higher angular basis functions ($f$-type etc.) is important, especially for larger atoms. For Ne for instance they contribute about 10% to $E^V_{\mathrm{IEPA}}$ [7].

Concerning the additivity errors – i.e. those errors generated by simply adding up the pair correlation energies in the IEPA-scheme – our results should be in between the results of "spin-orbital pairs" [22, 27–29] and "symmetry-adapted pairs" [18, 23].

## 3. Excitation Energies, Ionization Potentials and Electron Affinities

In all chemical applications relative energies are much more important than absolute energy values. We have therefore calculated excitation energies, first ionization potentials and electron affinities of first row atoms in order to investigate how reliable our spin-adapted IEPA results for the corresponding properties of first row hydrides are, at least for those for which a localization of the occupied SCF-orbitals is possible. In all cases the basis sets described in the previous section have been used.

The results of these calculations are given in Table 2 (excitation energies from the ground states) and Table 3 (first ionization potentials (IP) and electron affinities (EA)). We have added for comparison not only the experimental values – as far as available – but also the results of some previous more elaborate calculations, most of them based on the "naive" or symmetry-adapted IEPA scheme, but with atomic basis sets.

Table 2. Excitation energies from the ground state for some low-lying excited states of first row atoms (all energies in a.u.)

| Atom | Excited state | $E_{SCF}$ | $E_{SCF}+E^V_{IEPA}$ | exp. [35] | other calculations |
|---|---|---|---|---|---|
| Be | $^3P_u$ | 0.0621 | 0.1020 | 0.1001 | |
| B | $^4P_g$ | 0.0790 | 0.1318 | 0.1313 | |
| C | $^1D_g$ | 0.0876 | 0.0412 | 0.0464 | 0.0478 [49]<br>0.0485 [22]<br>0.0535 [23]<br>0.0469 [17] |
| | $^1S_g$ | 0.0876 | 0.1014 | 0.0986 | 0.0996 [49]<br>0.1053 [23]<br>0.1008 [17] |
| | $^5S_u$ | 0.0909 | 0.1516 | 0.1537 | 0.1501 [17] |
| N | $^2D_u$ | 0.1395 | 0.0963 | 0.0876 | 0.0912 [22]<br>0.0934 [23] |
| O | $^1D_g$ | 0.1255 | 0.0792 | 0.0723 | 0.0721 [22]<br>0.0760 [23] |
| | $^5S_u$ | 0.2807 | 0.3151 | 0.3361 | |
| F | $^4P_g$ | 0.4102 | 0.4484 | 0.4675 | |
| Ne | $^3P_u$ | 0.5528 | 0.5954 | 0.6105 | |

Table 3. First ionization potentials (IP) and electron affinities (EA) of first row atoms (in eV)

| Atom | | SCF | SCF | Koopmans' theorem | | SCF | corrected for | EA | exp. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | this work | Clementi [34] | this work | Clementi [34] | $+E^V_{IEPA}$ | K-L-interact. | Edlén [50] | | |
| Li | IP | 5.341 | 5.342 | 5.341 | 5.342 | 5.341 | 5.406 | | 5.390 | [35] |
| | EA | − 0.122 | − 0.122 | | | 0.589 | 0.654 | 0.82 | 0.6 | [51] |
| | | | | | | | | | 0.65...1.05 | [52] |
| Be | IP | 8.044 | 8.046 | 8.413 | 8.415 | 9.262 | 9.34 | | 9.320 | [35] |
| | EA | | | | | | | −0.19 | | |
| B | IP | 7.920 | 7.932 | 8.411 | 8.432 | 8.145 | 8.23 | | 8.296 | [35] |
| | EA | − 0.274 | − 0.268 | | | 0.243 | 0.32 | 0.33 | | |
| C | IP | 10.771 | 10.786 | 11.760 | 11.791 | 11.147 | 11.23 | | 11.264 | [35] |
| | EA | 0.547 | 0.549 | | | 1.322 | 1.40 | 1.24 | 1.25±0.03 | [53] |
| N | IP | 13.954 | 13.957 | 15.41 | 15.44 | 14.403 | 14.48 | | 14.54 | [35] |
| | EA | − 2.030 | − 2.150 | | | − 0.299 | − 0.22 | 0.05 | | |
| O | IP | 11.934 | 11.885 | 14.22 | 17.19 | 13.268 | 13.35 | | 13.614 | [35] |
| | EA | − 0.518 | − 0.541 | | | 1.505 | 1.59 | 1.47 | 1.465+0.005 | [54] |
| F | IP | 15.704 | 15.718 | 18.45 | 19.86 | 17.271 | 17.35 | | 17.42 | [35] |
| | EA | 1.342 | 1.363 | | | 3.621 | 3.70 | 3.50 | 3.398+0.002 | [55] |
| Ne | IP | 19.811 | 19.846 | 22.98 | 23.14 | 21.518 | 21.60 | | 21.559 | [35] |
| | EA | | | | | | | −0.57 | | |

We first note that our SCF-results for IP and EA are rather close to Clementi's near Hartree-Fock results [34] despite of our much poorer absolute SCF energies (see Table 1). The same holds for the IP values estimated according to Koopman's theorem [36] expect for those cases (O and F) where our radially unrestricted ground state wavefunction allows for two different IP's from the $2p$-shell which are closer to the experimental first two IP's than Clementi's value. But this is just an artefact of our calculation.

Generally SCF values for excitation energies as well as for IP's and EA's are in error by 1–2 eV for all first row atoms, the error increasing slightly with nuclear charge. Our IEPA treatment reduces these errors by about one order of magnitude, the remaining errors are in the order of 0.0–0.3 eV. For the small atoms up to carbon where the higher terms ($l > 2$) do not contribute very much to the correlation energy and where the number of individual pair contributions is small, the agreement with experiment is even better. Results of calculations with a spin- and symmetry-adapted IEPA scheme [20–23] for the same properties using extended STO-basis sets have still lower errors of up to 0.02 eV. But the rather high accuracy of IEPA-results seems to be partly due to a cancellation of errors (mainly deficiencies of the basis against additivity errors) such that even our modest IEPA calculations are superior to the large scale CI calculations of Sasaki and Yoshimine [17] as far as the quantitative agreement of properties like EA or IP with experiment is concerned.

Some remarks have to be added concerning the states $^1D_g$ and $^1S_g$ of carbon. For both states we started from the one-determinant configuration $1s^2 2s^2 2p_x^2$ regarding the determinants $1s^2 2s^2 2p_y^2$ and $1s^2 2s^2 2p_z^2$ as doubly substituted PNO configurations. Hence the "SCF" excitation energies for the two states are the same and it needs the pair-CI for the pair $p_x^2$ to split this degeneracy. The PNO's $p_y$ and $p_z$ are obtained with exactly or almost exactly the same radial form as $p_x$, which is a check for the accuracy of the determination of PNOs. Of course the whole difficulty disappears if one starts from many-determinant SCF wavefunctions.

## 4. Relative Energy Values for Small Carbon Hydrides

The present atomic calculations have been performed mainly to check the reliability of our IEPA results on molecules. Table 4 therefore contains a collection of results for energy differences of small carbon hydrides, part of them published previously [12, 13, 15]. Since in all cases the open-shell orbitals are almost completely localized on the carbon atom and the closed-shell orbitals can be localized without difficulty as well, we are sure that our conclusions drawn for atoms are valid also in this case.

Comparison with experiment shows that in fact the results of our IEPA calculations are reliable to about 0.1–0.3 eV. But one has to be aware of the fact that many of the experimental values have errors of the same order of magnitude, mainly since the species under consideration are very short-living. As we have pointed out previously [15] the experimental value for the electron affinity of $CH_3$ [37] seems to be almost 1 eV too high. Recent photodetachment measure-

Table 4. Energetic properties of small carbon hydrides (all energies in eV)

| Molecule | Property | our calculation | | exp. | | further calculations |
|---|---|---|---|---|---|---|
| | | SCF | IEPA | | | |
| C | PA[ac] | 5.95 | 6.86 | 5.99 | [47] | |
| CH | IP (vertical) | 10.02 | 10.20 | | | |
| | PA[a] | 8.17 | 7.83 | 7.58 | [47] | |
| | BE[b]($D_0$) | 2.21 | 3.30 | 3.47 | [39, 40] | 3.35 [41], CI |
| $CH_2$ [12] | IP (vertical) | 9.58 | 10.27 | 10.396 | [45] | |
| | $E(^3B_1)-E(^1A_1)$ | − 1.08 | − 0.39 | − 0.35 | [42] | −0.48 [43], CI |
| | BE[b] | 6.29 | 7.68 | 7.81±0.22 | [44] | |
| | PA[a] | 10.59 | 8.68 | 8.64 | [47] | |
| $CH_3$ [15] | IP (vertical) | 8.86 | 9.83 | 9.84 | [45] | |
| | EA (ad.) | − 1.38 | 0.11 | 1.1 | [37] | |
| | BE[b] | 9.71 | 12.27 | 12.62 | [40, 45] | |
| $CH^+$ | BE[b] | 2.98 | 4.18 | 4.04 | [46] | 3.94 [48], CI |

[a] Proton affinity.

[b] Binding energy; the calculated values are corrected for the zero point energy.

[c] Other properties compare Tables 2 and 3.

ments on similar molecules [38] support this suggestion. Analogously, the experimental values of the proton affinities which are based on thermochemical data [47] are quite uncertain, particularly the heats of formation of $CH^+$ and $CH_2$ have rather large errors.

## References

1. Ahlrichs, R., Kutzelnigg, W.: J. Chem. Phys. **48**, 1819 (1968)
2. Jungen, M., Ahlrichs, R.: Theoret. Chim. Acta (Berl.) **17**, 339 (1970)
3. Meyer, W.: Intern. J. Quantum Chem. **S 5**, 341 (1971)
4. Meyer, W.: J. Chem. Phys. **58**, 1017 (1973)
5. Meyer, W., Theoret. Chim. Acta (Berl.) **35**, 277 (1974)
6. Ahlrichs, R., Lischka, H., Staemmler, V., Kutzelnigg, W.: J. Chem. Phys. **62**, 1225 (1975)
7. Ahlrichs, R., Driessler, F., Lischka, H., Staemmler, V., Kutzelnigg, W.: J. Chem. Phys. **62**, 1235 (1975)
8. Kutzelnigg, W.: Molecular calculations including electron correlation. In: Clementi, E. (Ed.): Selected topics in molecular physics, p. 91. Weinheim: Verlag Chemie 1972
9. Kutzelnigg, W.: Electron correlation and electron pair theories. Topics in Current Chemistry, Vol. 41, p. 31. Berlin, Heidelberg, New York: Springer 1973
10. Van der Velde, G. A., Nieuwport, W. C.: Chem. Phys. Letters **13**, 409 (1972)
11. Staemmler, V., Jungen, M.: Chem. Phys. Letters **16**, 187 (1972)
12. Staemmler, V.: Theoret. Chim. Acta (Berl.) **31**, 49 (1973)
13. Staemmler, V.: Theoret. Chim. Acta (Berl.) **35**, 309 (1974)
14. Mehler, E. L.: Theoret. Chim. Acta (Berl.) **35**, 17 (1974)
15. Driessler, F., Ahlrichs, R., Staemmler, V., Kutzelnigg, W.: Theoret. Chim. Acta (Berl.) **30**, 315 (1973)
16. Staemmler, V.: Habilitationsschrift, Bochum 1975
17. Sasaki, F., Yoshimine, M.: Phys. Rev. **A 9**, 17, 26 (1974) and Refs. therein
18. Viers, J. W., Harris, F. E., Schaefer, III, H. F.: Phys. Rev. **A 1**, 24 (1970)
19. Barr, T. L., Davidson, E. R.: Phys. Rev. **A 1**, 644 (1970)
20. Weiss, A. W.: Phys. Rev. **A 3**, 1 (1971)
21. Marchetti, M. A., Krauss, M., Weiss, A. W.: Phys. Rev. **A 5**, 2387 (1972)

22. Moser, C. M., Nesbet, R. K.: Phys. Rev. **A 4**, 1336 (1971)
23. Moser, C. M., Nesbet, R. K.: Phys. Rev. **A 6**, 1710 (1972)
24. Davidson, E. R., Bender, C. F.: J. Chem. Phys. **49**, 465 (1968)
25. Bender, C. F., Davidson, E. R.: Chem. Phys. Letters **3**, 33 (1969)
26. Davidson, E. R., Bender, C. F.: J. Chem. Phys. **56**, 4334 (1972)
27. Nesbet, R. K.: Phys. Rev. **155**, 51 (1967)
28. Nesbet, R. K.: Phys. Rev. **155**, 56 (1967)
29. Nesbet, R. K.: Phys. Rev. **175**, 2 (1968)
30. Silverstone, H. J., Sinanoğlu, O.: J. Chem. Phys. **44**, 1889, 3608 (1966)
31. Sinanoğlu, O.: Advan. Chem. Phys. **14**, 237 (1969)
32. Jungen, M.: Theoret. Chim. Acta (Berl.) **11**, 193 (1968)
33. Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965)
34. Clementi, E.: Tables of atomic functions. IBM J. Res. Develop. Suppl. to **9**, 2 (1965)
35. Moore, C. E.: Atomic energy levels. Ntl. Bur. Std. (US), Circ. No. 467. Washington D.C.: US Government Printing Office 1949
36. Koopmans, T.: Physica **1**, 104 (1934)
37. Page, P. M., Goode, P. C.: Negative ions and the magnetron. London: Wiley-Interscience 1969
38. Celotta, R. J., Bennett, R. A., Hall, J. L.: J. Chem. Phys. **60**, 1740 (1974)
39. Herzberg, G.: Spectra of diatomic molecules. New York: Van Nostrand 1950
40. Gaydon, A. G.: Dissociation energies and spectra of diatomic molecules. London: Chapman and Hall 1968
41. Lie, G. C., Hinze, J., Liu, B.: J. Chem. Phys. **59**, 1872, 1887 (1973)
42. Frey, H. M.: J. Chem. Soc. Chem. Commun. 1024 (1972)
43. Bender, C. F., Schaefer, III, H. F., Franceschetti, D. R., Allen, L. C.: J. Am. Chem. Soc. **94**, 6888 (1972)
44. Prophet, H.: J. Chem. Phys. **38**, 2345 (1963)
45. Herzberg, G.: Electronic spectra of polyatomic molecules. New York: Van Nostrand 1967
46. Herzberg, G., Johns, J. W. C.: Astrophys. J. **158**, 399 (1969)
47. Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schuman, R. H.: Selected values of chemical thermodynamic properties. NBS Technical Note 270-3, 1968
48. Green, S., Bagus, P. S., Liu, B., McLean, A. D., Yoshimine, M.: Phys. Rev. **A 5**, 1614 (1972)
49. Weiss, A. W.: Phys. Rev. **162**, 71 (1967)
50. Edlen, B.: J. Chem. Phys. **33**, 98 (1960)
51. Ya'akobi, B.: Phys. Letters **23**, 655 (1966)
52. Scheer, M. D., Fine, J.: J. Chem. Phys. **50**, 4343 (1969)
53. Seman, M., Branscomb, L. M.: Phys. Rev. **125**, 1602 (1962)
54. Branscomb, L. M., Burch, D. S., Smith, S. J., Geltman, S.: Phys. Rev. **111**, 504 (1958)
55. Milstein, R., Berry, R. S.: J. Chem. Phys. **55**, 4146 (1971)

Dr. V. Staemmler
Lehrstuhl für Theoretische Chemie
Ruhr-Universität Bochum
D-463 Bochum-Querenberg,
Universitätsstraße 150
Postfach 2148
Federal Republic of Germany