Ab initio CALCULATIONS OF THE GROUND STATE POTENTIAL FUNCTION OF THE HYDROXYL ANION BY MEANS OF THE MANY-BODY RAYLEIGH–SCHRÖDINGER PERTURBATION THEORY

Ivan KOZÁK[a], Vladimír ŠPIRKO[b] and Petr ČÁRSKY[b]

[a] *INORGA, 040 01 Košice and*
[b] *J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Prague 2*

Many-body Rayleigh–Schrödinger perturbation theory (MB-RSPT) up to third order is applied to OH^- in the range of interatomic distances from 0·0815 to 0·1175 nm. The energy data obtained are combined with the experimental RKR (ground state) potential of HF, and, a ground state potential of OH^- is constructed (over a wide range of internuclear distances) within the framework of the reduced potential curve method. With the use of this potential the corresponding rotation-vibration Schrödinger equation is solved for $^{16}OH^-$. The computed spectroscopic constants are compared with best reported calculations and available experimental evidence. The comparison indicates that MB-RSPT may be used as an adequate (and convenient) tool for the study of negative ions.

In contrast to neutral species, the experimental determination of spectroscopic constants of negative ions is not straightforward and in spite of a recent progress in photo-detachment spectroscopy[1], experimental information for many negative ions is still fragmentary and uncertain. Also application of *ab initio* calculations to negative species is more difficult than it is with neutral molecules. Attachment of an extra loosely bound electron brings about an expansion of molecular orbitals, so that a larger basis set must be used. Also a coverage of the correlation energy becomes more difficult. For this reason the number of theoretical papers on negative ions is rather limited. For OH^- a near Hartree–Fock potential curve was published[2] as early as in 1967, but a large-scale beyond Hartree–Fock treatment was reported[3] more than a decade later. Other recent beyond Hartree–Fock calculations on OH^- were restricted to the evaluation of the electron affinity of the OH radical[4−6] and the proton affinity of the OH^- ion[7]. Recently many-body perturbation theory was applied[8] with success to potential curves of neutral closed-shell molecules. The aim of this paper is to provide further evidence on the utility of the perturbation theory and its possible applicability to negative ions. Available experimental data and above noted CEPA calculations[3] are used as standards, against which the results of perturbation calculations are judged.

CALCULATIONS

Basis set. The basis sets developed for neutral species have to be augmented with diffuse functions[9] when applied to negative ions. We assumed a single additional set of p-type gaussians with the exponent of 0·059, as suggested by Dunning and Hay[9]. The underlying set was Dunning's $(9s5p/4s)/[4s2p/2s]$ set[10] for oxygen and hydrogen, which was augmented with a single set of six d-functions on oxygen and a single set of p-functions on hydrogen. The exponent of hydrogen p-functions was fixed at $\alpha_p = 1·0$, whereas for oxygen we used $\alpha_d = 0·55$ which is the optimum d-exponent[11] for OH^-. The whole basis set may therefore be denoted as $(9s6p1d/4s1p)/[4s3p1d/2s1p]$.

Perturbation calculations. These were of Møller-Plesset type, following all details of the many--body Rayleigh–Schrödinger perturbation theory (MB-RSPT) through third order[12]. Actual calculations were performed on EC 1040 and EC 1033 computers using the program written by Urban and Kellö[8], which is compatible with the POLYATOM/2 program[13].

Potential function of OH^-. In applications to potential curves, MB-RSPT is known[8] to reproduce well the "experimental" potential curve for interatomic distances shorter than the equilibrium bond length (R_e) and for distances slightly longer than R_e, say $R < R_e + 0·3 . 10^{-10}$ m. At longer distances MB-RSPT breaks down. For this reason we selected for MB-RSPT calculations only a few points that were anticipated to lie relatively close to R_e (in R/a_0, $a_0 = 0·52917706$. $. 10^{-10}$ m): 1·54, 1·55, 1·62, 1·72, 1·82, 2·02 and 2·22. In order to have a realistic potential curve in the whole range of R, an extrapolation was made by means of the reduced potential curve method[15] with the use of the experimental RKR potential of HF (ref.[16]). A cubic spline fit[17] to the energy data obtained is used to get a continuous representation of the potential and the corresponding radial Schrödinger equation is solved for OH^- by means of Numerov's method[18].

TABLE I

Survey of selected calculations on OH^-

Calculation	Basis set	Energy[a,b]	Ref.
SCF	$(9s5p1d/4s1p)/[4s2p1d/2s1p]$	$-75·37283^c$	7
SCF	$(10s5p1d1f/4s1p)/[4s2p1d1f/2s1p]$	$-75·37070^d$	14
SCF	$(9s6p1d/4s1p)/[4s3p1d/2s1p]$	$-75·40093^e$	*f*
SCF	$(12s6p2d1f/6s2p1d)/[10s4p2d1f/4s2p1d]$	$-75·41448$	3
SCF	$(5s4p2d1f/3s1p)$ STO	$-75·41754$	2
MB-RSPT	$(9s6p1d/4s1p)/[4s3p1d/2s1p]$	$-75·61089$	*f*
PNO-CI	$(12s6p2d1f/6s2p1d)/[10s4p2d1f/4s2p1d]$	$-75·67423^g$	3
CEPA	$(12s6p2d1f/6s2p1d)/[10s4p2d1f/4s2p1d]$	$-75·69325^g$	3

^{a} Expressed in dimensionless quantities E/E_h, $E_h = 2\ 625·5$ kJ mol^{-1}; ^{b} If not otherwise noted, the energies refer to respective potential minima; ^{c} Computed for $R/a_0 = 1·845$; ^{d} Computed for $R/a_0 = 1·8$; ^{e} Computed for $R/a_0 = 1·82$; ^{f} this paper; ^{g} The oxygen $1s$ orbital was held doubly occupied.

RESULTS AND DISCUSSION

In Table I we present a comparison of our SCF and MB-RSPT energies of OH^- with the results of selected previous calculations. The first two lines of Table I show clearly that basis sets without diffuse p-functions give poor results, even if they are augmented by several polarization functions. The entries of Table I also conform to another known fact *viz.* that the computed correlation energy is affected by a basis set extension considerably more than the SCF energy. The summary of our calculations is given in Table II. In Table III we present a comparison of the obtained spectroscopic constants with the results of the most sophisticated calculations reported in the literature and the available experimental information. The observed value for R_e is reproduced by our MB-RSPT calculation within the experimental error. The perfect agreement should not be overestimated, however, because it may be due to a fortuitous cancellation of two effects: the effect of the limited basis set and the effect of the truncation of the MB-RSPT expansion at third order. It should be noted, however, that also similar calculations on the HF molecule[20] gave perfect agreement with experiment for the internuclear distance and that the predicted R_e converged rapidly to the experimental value as the order of the perturbation expansion was increased. It also should be noted that the discrepancy between CEPA and experiment is surprisingly large. For the vibrational frequency we have no experimental evidence. Assuming the CEPA value as a standard, the MB-RSPT prediction appears to be superior to that given by PNO-CI. Potential curves given by MB-RSPT cannot be used directly for the determination of dissociation energies,

TABLE II

SCF Energy and second-order (E_2) and third-order (E_3) perturbation contributions[a] to the correlation energy of OH^-

R/a_0	E_{SCF}/E_h	E_2/E_h	E_3/E_h	$(E_{SCF} + E_2 + E_3)/E_h$
1·54	−75·37265	−0·20812	0·00493	−75·57583
1·55	−75·37515	−0·20848	0·00503	−75·57860
1·62	−75·38882	−0·21091	0·00570	−75·59403
1·72	−75·39890	−0·21432	0·00665	−75·60656
1·82	−75·40093	−0·21739	0·00751	−75·61082
1·8374	−75·40066	−0·21786	0·00763	−75·61089
2·02	−75·39025	−0·22202	0·00860	−75·60366
2·22	−75·36959	−0·22513	0·00886	−75·58586

[a] Bond lengths and energies are expressed as dimensionless quantities, $a_0 = 0.52917706 \cdot 10^{-10}$ m, $E_h = 2626.5$ kJ mol^{-1}.

TABLE III

Molecular and Spectroscopic Constants for the Ground Electronic State of $^{16}OH^-$

Calculation	R_e, 10^{-10} m	B_e, cm^{-1}	α_e, cm^{-1}	ω_e, cm^{-1}	$\omega_e x_e$, cm^{-1}	D_0, cm^{-1}	Ref.
SCF	0·953	19·56	0·729	4 045	92	44 990	[b]
near Hartree–Fock	0·943	19·98	0·748	4 069	92	25 650	[3]
near Hartree–Fock	0·942	20·02	0·722	4 088	88	28 100[c]	[2]
SCF + E_2	0·979	18·15	0·612	3 782	74	50 500	[b]
SCF + E_2 + E_3	0·972	18·79	0·704	3 860	88	42 730	[b]
PNO–CI	0·956	19·46	0·740	3 903	93	35 890	[3]
CEPA	0·961	19·23	0·766	3 809	94	37 260	[3]
Experiment	0·971 ± 0·001	—	—	—	—	38 470	[19]

[a] E_2 and E_3 refer to second and third order of MB-RSPT; [b] this paper; [c] Separated atoms result.

because at longer interatomic distances MB-RSPT breaks down[8]. A reasonable estimate of D_0 may be obtained, however, if MB-RSPT data near R_e are combined with the reduced potential. It may concluded that the level of sophistication presented in this paper may be useful in applications to spectroscopic constants, since, with negative ions, its accuracy is only rarely achieved experimentally.

REFERENCES

1. Corderman R. R., Lineberger W. C.: Annu. Rev. Phys. Chem. *30*, 347 (1979).
2. Cade P. E.: J. Chem. Phys. *47*, 2390 (1967).
3. Rosmus P., Meyer W.: J. Chem. Phys. *69*, 2745 (1978).
4. Meyer W.: Theor. Chim. Acta *35*, 277 (1974).
5. Smith W. D., Chen T. T., Simons J.: Chem. Phys. Lett. *27*, 499 (1974).
6. Cederbaum L. S., Schönhammer K., von Niessen W.: Phys. Rev. *A15*, 833 (1977).
7. Lischka H., Čársky P., Zahradník R.: Chem. Phys. *25*, 19 (1977).
8. Urban M., Kellö V.: Mol. Phys. *38*, 1621 (1979).
9. Dunning T. H., jr, Hay P. J. in the book: *Modern Theoretical Chemistry* (H. F. Schaefer III, Ed.). Plenum Press, New York 1977.
10. Dunning T. H., jr: J. Chem. Phys. *53*, 2823 (1970).
11. Urban M., Kellö V., Čársky P.: Theor. Chim. Acta *45*, 205 (1977).
12. Paldus J., Čížek J.: Advan. Quant. Chem. *9*, 105 (1975).
13. Neumann D. B., Basch H., Kornegay R. L., Snyder L. C., Moskowitz J. W., Hornback C., Liebman S. P.: POLYATOM (Version 2). Quantum Chemistry Program Exchange No 199. Indiana University, Bloomington, Indiana.
14. Kari R., Csizmadia I. G.: Int. J. Quantum Chem. *11*, 441 (1977).
15. Jenč F., Plíva J.: This Journal *28*, 1449 (1963).
16. Di Lonardo G., Douglas A. E.: Can. J. Phys. *51*, 434 (1973).
17. Reinsch C. H.: Numer. Math. *10*, 177 (1967).
18. Cooley J. W.: Math. Comp. *15*, 363 (1961).
19. Hotop H., Patterson T. A., Lineberger W. C.: J. Chem. Phys. *60*, 1806 (1974).
20. Kellö V.: Chem. zvesti, in press.

Translated by the author (P. Č.).