Orbital Binding Energies within the Statistical Exchange Approximation: Ne and Ar Isoelectronic Series

K. D. Sen

Physikalische Chemie III, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, D-6100 Darmstadt, West Germany

Z. Naturforsch. **34a**, 901–902 (1979); received May 16, 1979

Binding energies are calculated using the orbital energies within the Kohn-Sham-Gaspar statistical exchange approximation for the Ne and Ar isoelectronic series, respectively. The results are generally in good agreement with the available Hartree-Fock orbital energies.

Slater and Wood [1] have shown that within the statistical exchange approximation the eigenvalue $\varepsilon_k{}^{X\alpha}$ differs from the orbital binding energy ε_k by the self interaction term of the kth orbital according to

$$\varepsilon_k = -\varepsilon_k{}^{X\alpha} + \tfrac{1}{2}\langle k||k\rangle, \qquad (1)$$

where the self interaction integral (in Rydbergs) is defined as

$$\langle k||k\rangle = \int_0^\infty u_k{}^*(1)\, u_k(1)\, g_{12}\, u_k{}^*(2)\, u_k(2)\, \mathrm{d}\tau_1\, \mathrm{d}\tau_2\,. \qquad (2)$$

Gopinathan [2] has recently derived (1) in a straightforward manner without assuming the differentiability of total statistical energy with the occupation number. As has been recently pointed out [3] there is a tendency to misidentify ε_k with $\varepsilon_k{}^{X\alpha}$ and use the latter quantity as the unrelaxed binding energy of the kth orbital. In the present authors opinion such a situation arises because only a few calculations, mostly concerning the neutral atoms, have been reported [1–3] so far with the aim of numerically testing (1), and it is necessary to test the latter over a large variety of ions.

In this communication we have calculated $\varepsilon_k{}^{X\alpha}$ and $\langle k||k\rangle$ values using Kohn-Sham [4] exchange ($\alpha = 2/3$) for the Ne and A atoms and a few isoelectronic ions. The binding energy ε_k was calculated using (1) and compared with the available [5] Hartree-Fock (HF) orbital energy $\varepsilon_k{}^{HF}$. In Table 1 and 2 we have listed the values of $\varepsilon_k{}^{X\alpha}$, $\frac{1}{2}\langle k||k\rangle$, ε_k and $\varepsilon_k{}^{HF}$ for the isoelectronic series containing 10 and 18 electrons, respectively. The binding energy values calculated via (1) are in excellent agreement with the corresponding Hartree-Fock energy values. It is a simple matter to calculate the integrals $\langle k||k\rangle$, and it would be worthwhile to replace $\varepsilon_k{}^{X\alpha}$ values by ε_k in the standard computer codes [6] for the atomic and molecular calculations, using statistical exchange approximation.

Reprint requests to Dr. K. D. Sen, Physikalische Chemie, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, 6100 Darmstadt, West Germany.

0340-4811 / 79 / 0700-0901 $ 01.00/0

Table 1. The values (in Rydbergs) of Xα eigenvalues: $\varepsilon_k{}^{X\alpha}$; self interaction energy of kth orbital $\langle k||k\rangle$; the Xα-orbital energy ε_k according to Eq. (1) of the text, and the HF eigenvalues $-\varepsilon_k{}^{HF}$ for the Ne isoelectronic series.

Atom		Ne	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}
1 s	$-\varepsilon_k{}^{X\alpha}$	60.77	76.15	93.58	113.04	134.52	158.01	183.51
	$1/2\langle k\|\|k\rangle$	5.93	6.54	7.16	7.78	8.40	9.02	9.64
	$-\varepsilon_k$	66.70	82.69	100.74	120.82	142.92	167.03	193.14
	$-\varepsilon_k{}^{HF}$	65.54	81.51	99.54	119.58	141.64	165.72	191.81
2 s	$\varepsilon_k{}^{X\alpha}$	2.73	4.77	7.36	10.47	14.11	18.25	22.91
	$1/2\langle k\|\|k\rangle$	1.00	1.14	1.28	1.44	1.58	1.73	1.88
	$-\varepsilon_k$	3.73	5.91	8.64	11.91	15.69	19.98	24.79
	$-\varepsilon_k{}^{HF}$	3.86	6.14	8.96	12.30	16.14	20.50	25.36
2 p	$\varepsilon_k{}^{X\alpha}$	1.11	2.79	5.01	7.75	11.01	14.78	19.05
	$1/2\langle k\|\|k\rangle$	0.89	1.09	1.28	1.36	1.64	1.82	2.00
	$-\varepsilon_k$	2.00	3.88	6.29	9.11	12.65	16.60	21.05
	$-\varepsilon_k{}^{HF}$	1.70	3.59	5.78	8.94	12.38	16.32	20.78

Table 2. The values (in Rydbergs) of Xα eigenvalues: $-\varepsilon_k^{X\alpha}$, self interaction energy of kth orbital: $\langle k||k\rangle$, the Xα-orbital energy ε_k according to Eq. (1) of the text, and the HF eigenvalue $-\varepsilon_k^{HF}$ for the A isoelectronic series.

Atom		A	K^+	Ca^{2+}	Sc^{3+}	V^{5+}	Cr^{6+}
1 s	$-\varepsilon_k^{X\alpha}$	227.62	257.29	289.00	322.74	396.29	436.08
	$1/2\langle k\|\|k\rangle$	10.88	11.50	12.12	12.74	13.99	14.61
	$-\varepsilon_k$	238.50	268.79	301.12	335.48	410.28	450.69
	$-\varepsilon_k^{HF}$	237.22	267.50	299.83	334.18	408.94	449.35
2 s	$\varepsilon_k^{X\alpha}$	21.63	26.16	31.24	36.85	49.67	56.85
	$1/2\langle k\|\|k\rangle$	2.17	2.50	2.46	2.61	2.90	3.05
	$-\varepsilon_k$	23.80	28.66	33.70	39.46	53.57	59.90
	$-\varepsilon_k^{HF}$	24.64	29.41	34.74	40.59	53.86	61.28
2 p	$-\varepsilon_k^{X\alpha}$	16.93	21.05	25.71	30.92	42.90	49.66
	$1/2\langle k\|\|k\rangle$	2.34	2.50	2.68	2.85	3.19	3.37
	$-\varepsilon_k$	19.26	23.55	28.39	33.77	46.09	53.03
	$-\varepsilon_k^{HF}$	19.14	23.48	28.36	33.77	46.15	53.11
3 s	$-\varepsilon_k^{X\alpha}$	1.79	3.02	4.52	6.27	10.50	12.96
	$1/2\langle k\|\|k\rangle$	0.64	0.70	0.77	0.84	0.98	1.04
	$-\varepsilon_k$	2.43	3.72	5.29	7.11	11.48	14.01
	$-\varepsilon_k^{HF}$	2.55	3.93	5.56	7.43	11.86	14.45
3 p	$-\varepsilon_k^{X\alpha}$	0.80	1.86	3.18	4.75	8.62	10.90
	$1/2\langle k\|\|k\rangle$	0.05	0.59	0.52	0.75	0.90	0.98
	$-\varepsilon_k$	0.85	2.45	3.70	5.50	9.52	11.88
	$-\varepsilon_k^{HF}$	1.18	2.34	3.75	5.41	9.43	11.78

Acknowledgement.

KDS is grateful to the Alexander von Humbold fundation for an award of a fellowship and to the University of Hyderabad, India for a special grand of leave. He thanks Prof. Alarich Weiss for this interest in this worh.

[1] J. C. Slater and J. H. Wood, Intern. J. Quantum Chem. S **4**, 3 (1971).
[2] M. S. Gopinathan, J. Phys. B: Atom. Molec. Phys. **12**, 521 (1979).
[3] J. H. Wood, Chem. Phys. Lett. **51**, 582 (1977).
[4] W. Kohn and L. J. Sham, Phys. Rev. **140**, A 1133 (1965); R. Gaspar, Acta Phys. Hung. **3**, 263 (1954).
[5] E. Clementi and C. Roetti, At. Data and Nucl. Data Tab. **14**, 177 (1974).
[6] F. Herman and S. Skillman, Atomic Structure Calculations, Prentice Hall, New Jersey 1963.