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Citation: *The Journal of Chemical Physics* **78**, 4779 (1983); doi: 10.1063/1.445279

View online: <http://dx.doi.org/10.1063/1.445279>

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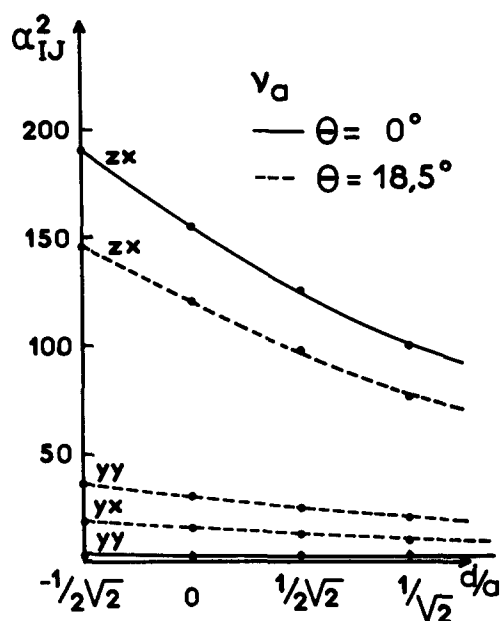


FIG. 3. Scattering activities of  $\nu_a(\text{C-C})$  in terms of  $d/a$ .

Thus, via a very simple reasoning permitting to keep control on the physical meaning of the problem, we have

been able to verify that (1)  $\alpha_{zz}^2$  is the greatest term for  $\nu_s(\text{C-C})$  and  $\alpha_{zx}^2$  for  $\nu_a(\text{C-C})$ , (Fig. 3); these results confirm the reversal of Liang's assignment<sup>5</sup> by Tasumi<sup>4</sup>; (2)  $\nu_a(\text{C-C})$  is not coupled with other vibrations.

The tilting of the chains (nearly 18°) agrees with the tilting of amphotericin included in phospholipid multilayers.<sup>6</sup>

<sup>1</sup>G. Masetti, S. Abbate, M. Gussoni, and G. Zerbi, *J. Chem. Phys.* **73**, 4671 (1980); S. A. Asher, R. Stearns, T. Urabe, and P. S. Pershan, *Mol. Cryst. Liq. Cryst.* **63**, 193 (1981).

<sup>2</sup>W. L. Peticolas, M. Harrand, and R. Dupeyrat, *J. Raman Spectros.* **12**, 130 (1982).

<sup>3</sup>M. Harrand, W. L. Peticolas, and R. Dupeyrat, *Biochem. Biophys. Res. Commun.* **104**, 1120 (1982).

<sup>4</sup>M. Tasumi, T. Shimanouchi, and T. Miyazawa, *J. Mol. Spectros.* **9**, 261 (1962).

<sup>5</sup>C. Y. Liang, S. Krimm, and G. B. B. M. Sutherland, *J. Chem. Phys.* **25**, 543 (1956).

<sup>6</sup>M. Masson, *Proceedings of the VIIIth International Conference on Raman Spectroscopy, Bordeaux*, edited by J. Lascombe and P. V. Huong (Wiley, Chichester, 1982), p. 247.

<sup>7</sup>M. Harrand, in *Proceedings of the VIIIth International Conference on Raman Spectroscopy, Bordeaux*, edited by J. Lascombe and P. V. Huong, (Wiley, Chichester, 1982), p. 571.

## NOTES

# Isoelectronic changes in the Hartree-Fock properties of atoms

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(Received 1 March 1982; accepted 10 May 1982)

The systematic variation of the Hartree-Fock (HF) estimates of the nuclear electron attraction energy  $V_{ne}$ , electron-electron repulsion energy  $V_{ee}$ , and the total electronic energy  $E^{\text{HF}}$ , respectively within an isoelectronic series of atoms has been noted in the literature.<sup>1-4</sup> Castro *et al.*<sup>5</sup> have shown using the  $Z^{-1}$  perturbation expansion<sup>6</sup> of  $E^{\text{HF}}$  that the second finite differences  $-D^2$  in  $E^{\text{HF}}$  remain constant within an isoelectronic series. In addition, a constant increment of 0.25 in  $-D^2$  in going from  $N$  to  $N+1$  electron series has been noted by these authors. The systematics in  $-D^2$  have been subsequently attributed<sup>7</sup> to the variation in  $\langle 1/r_1 \rangle$  within the series. The purpose of this communication is to report the result that the second differences in the eigenvalue sum  $\sum \nu_i \epsilon_i$  within an isoelectronic series display exactly the same systematics as those observed in the case of  $E^{\text{HF}}$ . Our result follows from the  $Z^{-1}$  expansion<sup>6,8,9</sup> of  $E^{\text{HF}}$ ,  $V_{ne}$ , and  $V_{ee}$  which may be written as

$$E^{\text{HF}} = \frac{1}{2} b Z^2 + a_1 Z + \frac{1}{2} a_0 + \dots, \quad (1)$$

$$V_{ne} = b Z^2 + a_1 Z + \dots, \quad (2)$$

$$V_{ee} = a_1 Z + a_0 + \dots, \quad (3)$$

respectively. Within the HF approximation Eqs. (1)–(3) lead<sup>10,11</sup> to

$$\sum \nu_i \epsilon_i = \frac{1}{2} b Z^2 + 2a_1 Z + 3/2 a_0 + \dots. \quad (4)$$

Note that the second differences in  $V_{ne}$  are predicted to be twice the  $-D^2$  corresponding to  $E^{\text{HF}}$  and  $\sum \nu_i \epsilon_i$ , respectively. The latter are found to be 2.00, 2.25, 2.50, and 2.75 a.u., etc., corresponding to the 2–10 electron series, respectively. Within the isoelectronic series defined by the filling up of the  $M$ -shell, the increment in  $-D^2$  in going from  $N$  to  $N+1$  isoelectronic series is found to be 0.111 a.u. For example, in the case of 11–14 electron series the  $-D^2$  values are given by 4.000, 4.111, 4.223, etc., respectively. This can

TABLE I. Comparison of the values of the coefficients in a three-term polynomial of  $E^{\text{HF}}$  in  $Z$  derived from Eqs. (1) and (2) and the values of  $V_{ne}$ ,  $E^{\text{HF}}$  corresponding to the neutral atom with the actual HF values obtained from the least squares fitting. All values are given in a.u. .

Isoelectronic series	$-b$		$a_1$		$-\frac{1}{2}a_0$	
	Present	HF	Present	HF	Present	HF
He	2.000	2.000	0.625	0.625	0.113	0.112
Li	2.250	2.250	1.032	1.028	0.403	0.389
Be	2.500	2.500	1.572	1.581	0.860	0.891
Ne	4.000	4.004	8.888	8.874	17.419	17.068
Na	4.111	4.116	9.797	9.770	20.876	20.272
Mg	4.223	4.228	10.754	10.732	24.616	23.945

<sup>a</sup>Average percentage error  $< 10^{-3}$ .

be explained on the basis of the systematic trend in the hydrogenlike term in the  $Z^{-1}$  expansion<sup>7,12,13</sup> of  $E^{\text{HF}}$ . Such a systematic trend in  $-D^2$ , although derived from the existing HF data,<sup>14</sup> can be used in turn to obtain reasonably good estimates of  $V_{ne}$ ,  $V_{ee}$ ,  $\sum \nu_i \epsilon_i$ , and  $E^{\text{HF}}$ , respectively within a given isoelectronic series simply from the calculations of  $V_{ne}$  and  $E^{\text{HF}}$  corresponding to the first member (neutral atom) of the series. Thus, using Eqs. (1) and (2), we have obtained the values of  $a_1$  and  $a_0$ , respectively from the estimates<sup>14</sup> of the  $E^{\text{HF}}$  and  $V_{ne}$  values corresponding to the He, Li, Be, Ne, Na, and Mg isoelectronic series, respectively and compared the results with the least-squares fit coefficients obtained from fitting a three-term polynomial for  $E^{\text{HF}}$  passing through the first 35 positive ions in each series. The results are listed in Table I. It is found that the presently estimated values of  $b$ ,  $a_1$ , and  $a_0$  are in good agreement with the fitted parameters. Using the present values of  $b$ ,  $a_1$ , and  $a_0$  we obtain the estimates of  $V_{ne}$ ,  $\sum \nu_i \epsilon_i$ , and  $E^{\text{HF}}$  corresponding to  $\text{Ar}^{16+}$  (He series) as  $-636.75$ ,  $-301.88$ , and  $-312.86$  a.u., respectively which compares well with the actual HF data given by  $-636.75$ ,  $-301.88$ , and  $-312.86$  a.u., respectively. The accuracy of the present method is of similar order in the other isoelectronic series considered here. For example, in the case of  $\text{Ar}^{8+}$  (Ne series) the estimated values of  $V_{ne}$ ,  $\sum \nu_i \epsilon_i$  and  $E^{\text{HF}}$  are given by  $-5679.95$ ,  $-2043.06$ , and  $-2574.34$  to be compared with the actual HF values of  $-5687.37$ ,  $-2044.64$ , and  $-2577.34$ , re-

spectively. In conclusion, the systematic trend in  $-D^2$  in  $E^{\text{HF}}$ ,  $\sum \nu_i \epsilon_i$ , and  $V_{ne}$  and the knowledge of the HF properties corresponding to just the first member in an isoelectronic series can be combined to obtain reasonably good estimates of the various HF properties within the series.

<sup>a</sup>Masters Thesis, School of Chemistry, University of Hyderabad.

<sup>1</sup>P. Politzer and D. G. Truhlar *Chemical Applications of Atomic and Molecular Electrostatic Potentials* (Plenum, New York, 1981).

<sup>2</sup>R. J. Boyd, J. Phys. B 11, L655 (1978).

<sup>3</sup>M. Cohen, J. Phys. B 12, L219 (1979).

<sup>4</sup>J. Largo-Cabrero, Chem. Phys. Lett. 70, 550 (1980).

<sup>5</sup>E. A. Castro, F. M. Fernandez, and J. Maronon, J. Phys. B 14, L477 (1981).

<sup>6</sup>P. O. Löwdin, J. Mol. Spectrosc. 3, 46 (1959); J. Lindenberg, Phys. Rev. 121, 816 (1961).

<sup>7</sup>K. D. Sen, J. Phys. B 14, L759 (1981); M. Levy, J. Chem. Phys. 68, 5298 (1978).

<sup>8</sup>G. G. Hall, Philos. Mag. 6, 249 (1961).

<sup>9</sup>P. Politzer and K. C. Daiker, Int. J. Quantum Chem. 14, 245 (1978).

<sup>10</sup>K. D. Sen, J. Phys. B 12, L287 (1979).

<sup>11</sup>G. I. Plindov and S. K. Pogrebnya, J. Phys. B 13, L281 (1980).

<sup>12</sup>D. Layzer, Ann. Phys. 8, 271 (1959).

<sup>13</sup>N. March and White, J. Phys. B 5, 466 (1972).

<sup>14</sup>E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974).