

## Hydrogen bonding between neon and water

M. Losonczy and J. W. Moskowitz\*

*Chemistry Department, New York University, Washington Square College, New York, New York 10003*

F. H. Stillinger

*Bell Laboratories, Murray Hill, New Jersey 07974*

(Received 10 May 1973)

Portions of the neon-water ground-state potential hypersurface have been mapped, using the Hartree-Fock approximation with an extensive Gaussian basis. A weak linear (OH  $\cdots$  Ne) hydrogen bond appears, with length 3.63 Å, and strength 0.17 kcal/mole. The analogous calculation for the argon-water pair predicts considerably less stabilization, in closer accord with pure electrostatic interaction of a permanent dipole moment (water molecule) and a polarizable particle (noble gas atom).

### I. INTRODUCTION

It is generally acknowledged that hydrogen bonding plays a fundamental role in structural chemistry and in the chemical basis of life. On account of that fact, broad scientific effort has long been devoted to examining substances which exhibit the phenomenon, and consequently a variety of review articles and textbooks devoted to hydrogen bonding are available.<sup>1</sup>

For the most part, explanations of hydrogen bonding seem to be after-the-fact rationalizations of established experimental observations, rather than expositions of deep theoretical logic with broad deductive power. We offer here a paradigm in the realm of hydrogen bonding which may stimulate a sharpening of future thought on the subject.

One of the more striking developments in the recent phase of structural chemistry has been the discovery of covalent noble gas compounds.<sup>2</sup> Having become acclimated to their existence, it then seems natural to inquire, by analogy, whether noble gases also engage in hydrogen bonding. Our results below affirm that possibility, but as one would naturally expect, the bond energy is very small by ordinary standards.

We have chosen the neon-water and argon-water systems for examination in this paper. In part, that choice stems from the burgeoning interest in quantum-mechanical calculations involving the water molecule<sup>3-4</sup> (thus permitting instructive comparisons with previous work). However, it also stems from an increasing capacity to probe the statistical mechanics of aqueous fluids.<sup>5</sup>

The computations reported here utilize the Hartree-Fock approximation for the ground state of the atom-molecule complexes. The following Sec. II describes the basis set employed, and specifies the geometric convention. Numerical results are gathered in Sec. III. The final Sec. IV discusses

some implications of the results, and suggests fruitful directions for further experimental and theoretical study.

### II. COMPUTATIONAL DETAILS

The computations were carried out at the N. Y. U. Computation Center on its CDC 6600, by means of POLYATOM (Version 2).<sup>6</sup> The basis functions utilized consist of gaussian atomic orbitals centered on the nuclei. For the water molecule, an extensive basis (including *d* orbitals on oxygen, and *p* orbitals on the hydrogens) was employed, which was identical to that of Ref. 4, and which conventionally is designated [531|21]. For Ne and Ar, comparable bases were constructed, with details shown in Table I. The ground-state energies for the separate species have the following values in atomic units:

$$\begin{aligned} \text{Ne:} & -128.515921, \\ \text{Ar:} & -526.799398, \\ \text{H}_2\text{O:} & -76.041319, \end{aligned} \quad (2.1)$$

where the last corresponds to OH bond length 0.945 Å, and bond angle 106°, the minimum energy configuration.

In view of the rigidity of the water molecule, we felt that interactions of that molecule with a noble gas atom would produce only minor distortions. Consequently the geometry of the isolated monomer (0.945 Å, 106°) was maintained throughout the calculations. With this restraint, the atom-molecule complex can be described with just three configurational coordinates. As Fig. 1 shows, we take these to be the distance (*R*) between the oxygen and gas atom nuclei, and two angles ( $\theta$  and  $\varphi$ ) to specify orientation.

### III. RESULTS

The numerical results for all of our calculations are gathered in Table II. In order to display the distance variation of the interaction energy for the neon-water pair, Fig. 2 provides curves passing through the relevant points from Table II for the following directions of approach of the gas atom:

TABLE I. Contracted Gaussian orbitals utilized for the noble gas atoms.

Atom	Type	Approximate orbital Representation	Coefficient	Exponent (a.u.)	
Ne	s	1s	1.0000	49.8918	
			0.6195	121.4484	
		1s'	1.0000	463.3183	
			0.1335	2268.7366	
			0.0323	7397.6730	
		1s''	1.8887	20.4890	
			1.0784	7.3344	
		2s	1.2228	1.5042	
			-0.1548	16.4005	
			1.0000	0.4501	
	p	2p	0.10164	12.9187	
			0.01632	56.4511	
		2p'	0.34961	0.34440	
		2p''	0.48583	1.20292	
			0.30927	3.86542	
			1.0000	1.40156	
	Ar	s	1s	0.00509438	130000.
				0.0435639	13095.
				0.19492144	3202.5
				0.8238022	914.001
1s'			0.21254172	287.988	
			0.41473296	102.797	
			0.39113245	40.1392	
			0.08912810	15.5983	
2s			-0.08498828	48.143667	
			0.43901055	7.459310	
		0.49000919	3.5013102		
		0.14886087	1.6953150		
		0.00504634	0.53304642		
p		2s'	-0.14665483	3.0631149	
			0.48904807	0.71342004	
			0.48406209	0.31137077	
			0.15481996	0.15380601	
		3s	0.15481996	0.15380601	
		2p		0.00434725	1237.25
				0.05154712	218.249
			0.26684514	63.2230	
			0.76604263	22.9254	
	2p'		0.48657832	9.47092	
	0.42953980		4.26463		
3p		0.15798810	2.06257		
		0.01648629	0.859474		
		0.16883989	1.51418644		
		0.43718600	0.65736877		
		0.39120125	0.26783188		
		0.14973805	0.11796413		
d	3p'	0.14973805	0.11796413		
	3d	1.0000000	2.01800		

(a) along an OH bond ( $\theta = 53^\circ$ ,  $\varphi = 0$ );

(b) frontal approach along the H<sub>2</sub>O symmetry axis ( $\theta = 0$ ,  $\varphi = 0$ );

(c) approach along the backside extension of the symmetry axis ( $\theta = 180^\circ$ ,  $\varphi = 0^\circ$ );

(d) approach from directly above the oxygen nucleus ( $\theta = 0$ ,  $\varphi = 90^\circ$ ).

The most important conclusion to be drawn from Fig. 2 is the relative preference for the complex (at least among the configurations shown) to have one of the water-molecule OH bonds pointing toward the Ne atom. For each of the directions shown, the potential passes through a single minimum near 3.5 Å, but the depth of the minimum obviously undergoes substantial variation as the angles change.

To clarify the angular preference of the potential, at least in the plane of the water molecule, several calculations were carried out at  $R = 3.731$  Å, near the minimum for curve 2(a). Figure 3 presents the potential variation as the Ne swings at this distance past the OH direction, in the molecular plane. Similarly, Fig. 4 gives the  $\varphi$  variation of the potential, at  $R = 3.731$  Å and  $\theta = 53^\circ$ , as the Ne atom moves upward out of the molecular plane.

The net result conveyed collectively by Figs. 2-4 is that a pair of equivalent distinctive minima in the pair potential exists along the OH bonds. It is appropriate tentatively to identify them as indicators of weak hydrogen bonds, considering the analogous propensity for linearity in more conventional hydrogen bonds.

A vivid way to present the configurational nature of the pair interaction involves a contour plot. Figure 5 exhibits such a plot for the plane of the water molecule ( $\varphi = 0$ ), prepared from data in Table II,

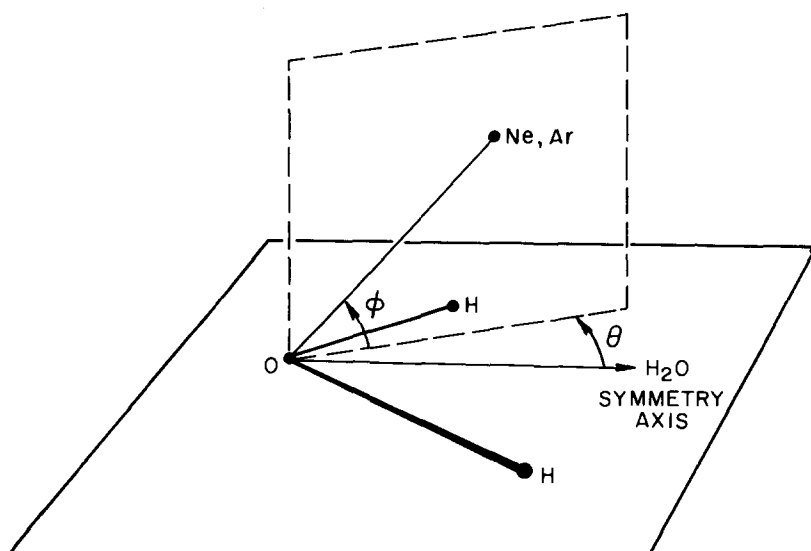


FIG. 1. Coordinate system used to describe the configuration of the water molecule-gas atom complex.

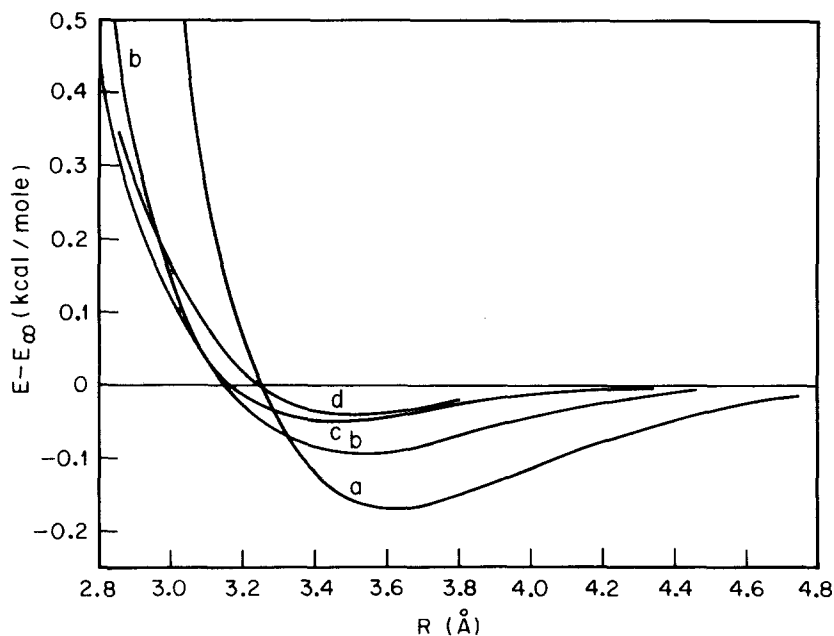


FIG. 2. Variation of ne-n-water interaction energy with distance. The curve designations follow the text of Sec. III.

TABLE II. Interaction energies for the water-noble gas complexes. The configurational variables refer to Fig. 1. The ground state energy is  $E$ , and its infinite separation limit is  $E_\infty$ .

System	$R$ (a.u.)	$R$ (Å)	$\theta$	$\varphi$	$E$ (a.u.)	$E - E_\infty$ (a.u.)	$E - E_\infty$ (kcal/mole)
Ne-H <sub>2</sub> O	5.615	2.971	53°	0°	-204.556057	0.00183	0.7426
	6.615	3.500	53°	0°	-204.557489	-0.000249	-0.1563
	7.051	3.731	53°	0°	-204.557495	-0.000255	-0.1601
	7.615	4.030	53°	0°	-204.557413	-0.000173	-0.1086
	8.615	4.559	53°	0°	-204.557283	-0.000043	-0.0270
	$\infty$	$\infty$	53°	0°	-204.557240	0.000000	0.0000
	5.000	2.646	180°	0°	-204.555566	0.001674	1.0508
	6.000	3.175	180°	0°	-204.557244	-0.000004	-0.0025
	7.000	3.704	180°	0°	-204.557291	-0.000051	-0.0320
	8.000	4.233	180°	0°	-204.557251	-0.000011	-0.0069
	5.000	2.646	0°	0°	-204.553957	0.003283	2.0608
	6.000	3.175	0°	0°	-204.557265	-0.000025	-0.0157
	7.000	3.704	0°	0°	-204.557370	-0.000130	-0.0816
	8.000	4.233	0°	0°	-204.557272	-0.000032	-0.0201
	5.000	2.646	0°	90°	-204.555043	0.002197	1.3791
	6.000	3.175	0°	90°	-204.557193	0.000047	0.0295
	7.000	3.704	0°	90°	-204.557286	-0.000046	-0.0289
	8.000	4.233	0°	90°	-204.557248	-0.000008	-0.0050
	7.051	3.731	15°	0°	-204.557390	-0.000150	-0.0942
	7.051	3.731	30°	0°	-204.557448	-0.000208	-0.1306
	7.051	3.731	45°	0°	-204.557491	-0.000251	-0.1576
	7.051	3.731	60°	0°	-204.557486	-0.000246	-0.1544
	7.051	3.731	90°	0°	-204.557377	-0.000137	-0.0860
	7.051	3.731	120°	0°	-204.557302	-0.000062	-0.0389
7.051	3.731	53°	30°	-204.557415	-0.000175	-0.1098	
7.051	3.731	53°	45°	-204.557351	-0.000111	-0.0697	
7.051	3.731	53°	60°	-204.557308	-0.000068	-0.0427	
7.051	3.731	53°	120°	-204.557285	-0.000045	-0.0282	
Ar-H <sub>2</sub> O	7.001	3.705	53°	0°	-602.840236	0.000482	0.3026
	7.736	4.094	53°	0°	-602.840679	0.000039	0.0245
	8.696	4.602	53°	0°	-602.840746	-0.000028	-0.0176
	9.756	5.163	53°	0°	-602.840731	-0.000013	-0.0082
	11.001	5.821	53°	0°	-602.840720	-0.000002	-0.0013
	12.785	6.765	53°	0°	-602.840718	0.000000	0.0000
	$\infty$	$\infty$	53°	0°	-602.840718	0.000000	0.0000

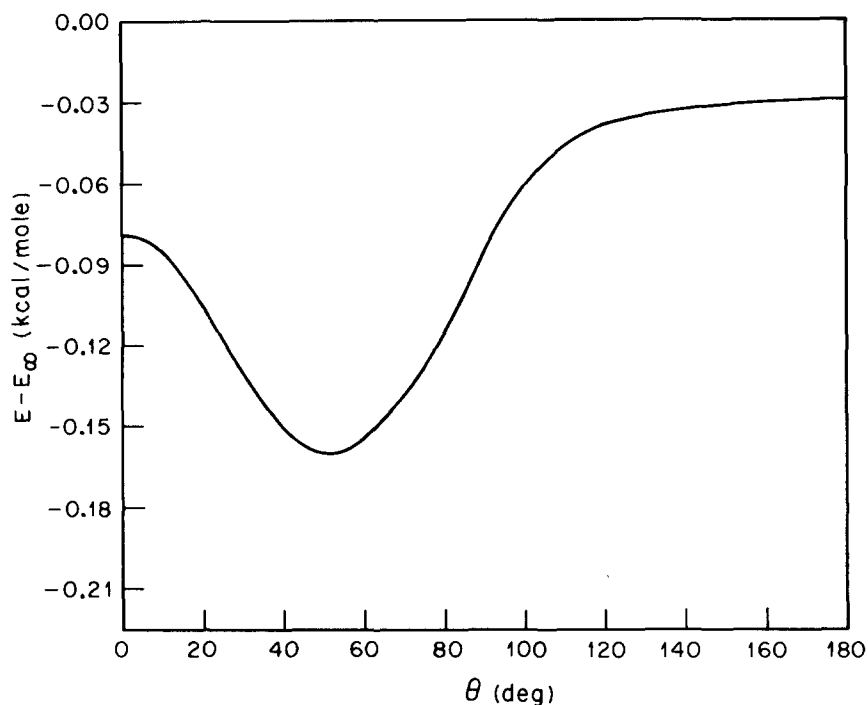


FIG. 3.  $\theta$  variation of Ne-H<sub>2</sub>O potential at  $R = 3.731 \text{ \AA}$ ,  $\phi = 0$ .

and the curves in Figs. 2 and 3. The localized minima along the OH bond directions are very obvious in this representation. From the available tabular and graphical information, we conclude that the minima occur at  $R = 3.63 \text{ \AA}$ ,  $\theta = \pm 53^\circ$ ,  $\phi = 0$ , and have energy  $-0.17 \text{ kcal/mole}$  compared to infinite separation.

The argon-water calculations were far more difficult to implement. As a result, only six points on the potential surface have been obtained, all of which are along the OH bond direction. Some of these points appear in Fig. 6, connected by a smooth curve. Not only has the minimum moved outward from  $3.63$  to  $4.45 \text{ \AA}$ , but its depth has di-

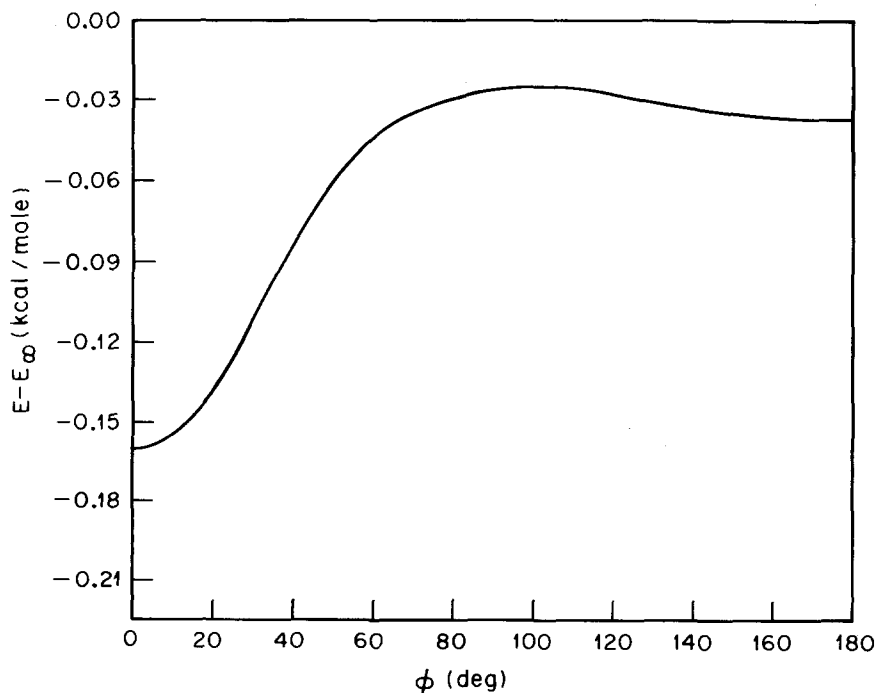


FIG. 4.  $\phi$  variation of Ne-H<sub>2</sub>O potential at  $R = 3.731 \text{ \AA}$ ,  $\theta = 53^\circ$ .

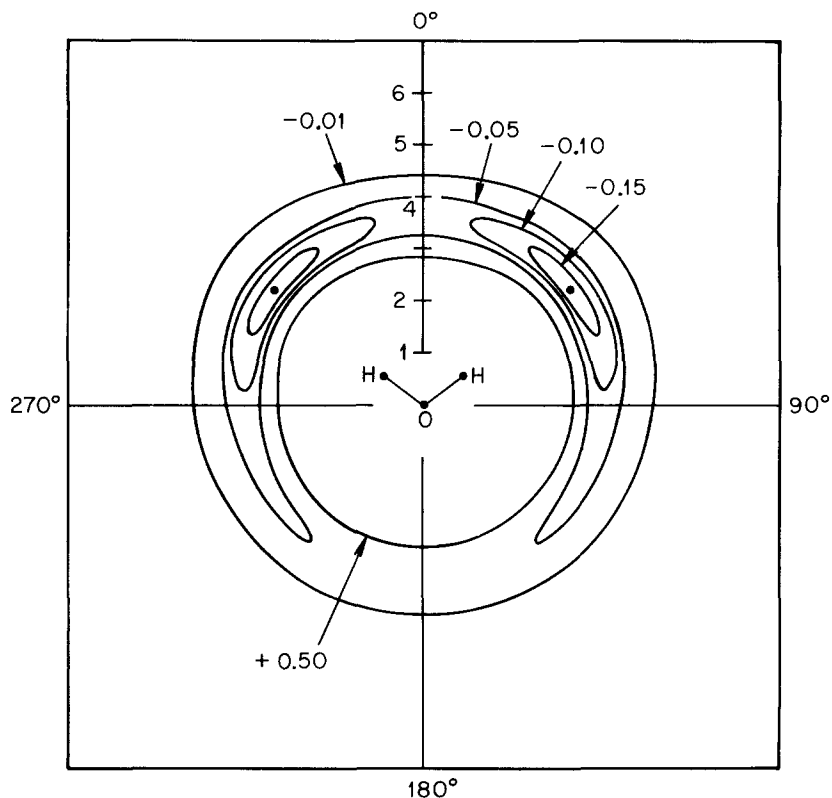


FIG. 5. Contour plot of the Ne-H<sub>2</sub>O interaction, in the  $\varphi=0$  molecular plane. The energy identifications are in kilocalories per mole.

minished in magnitude by a factor of about nine, to  $-0.02$  kcal/mole.

The question of whether or not localized minima exist along the OH bond directions with argon as with neon, must await further work. At least we can now draw the satisfying conclusion that the earlier observation<sup>1</sup> of weaker hydrogen-bonding

capacity for second-row elements compared to first-row elements can be extended to the noble gases.

That hydrogen bonds involve covalency and charge transfer has often been documented by calculated shifts in Mulliken populations, and overlaps, as the bonds form. Figure 7 presents the

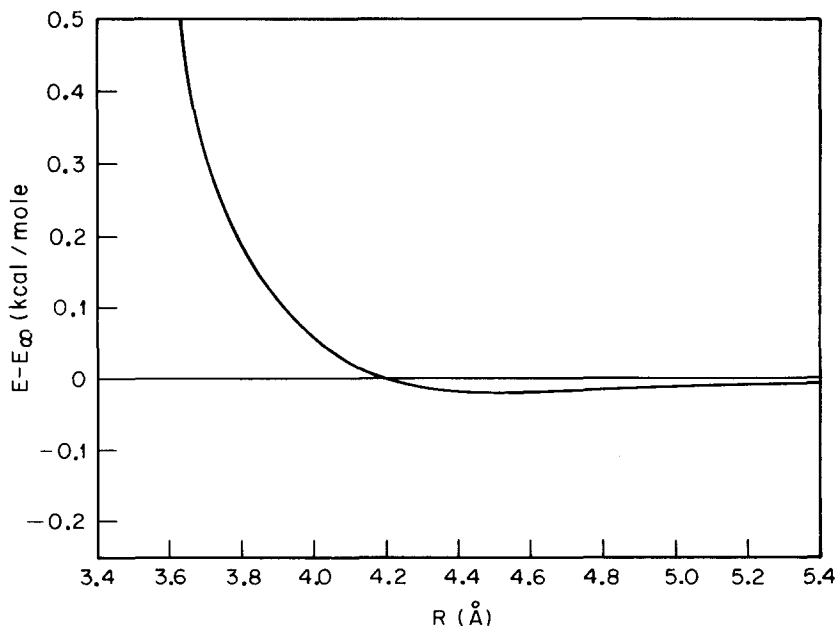


FIG. 6. Argon-water interaction potential variation along the OH bond direction ( $\theta=53^\circ$ ,  $\varphi=0$ ).

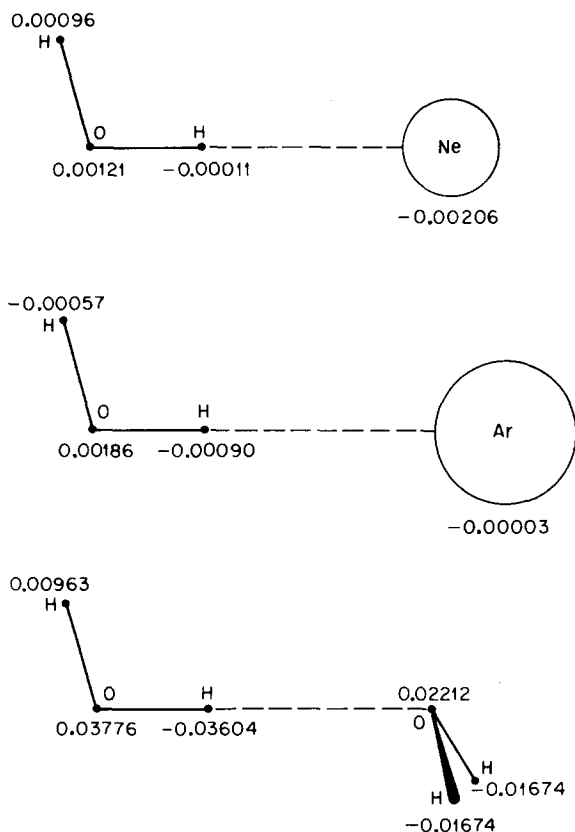


FIG. 7. Shifts in Mulliken populations induced by interaction. In each case the proton acceptor nucleus lies along the OH direction ( $\theta = 53^\circ$ ,  $\varphi = 0$ ) at the potential minimum for distance variation. Negative shifts represent fractional electron loss, positive shifts represent gains.

population shifts for the neon-water and argon-water complexes at the corresponding potential minima for  $\theta = 53^\circ$ ,  $\varphi = 0$  (linear hydrogen bond). Included as well for comparison is the water dimer in its symmetric linear hydrogen-bond configuration ( $R_{00} = 3.00 \text{ \AA}$ ).<sup>4,7</sup>

#### IV. DISCUSSION

The principal error in the calculations reported here stems from the inherent failure of the Hartree-Fock approximation to describe electron correlation properly. As a result, the potential energy surfaces obtained do not include London dispersion attractions. At, or beyond, the distance of the potential minima obtained in the previous Section, the inverse sixth-power dispersion interactions should provide an adequate estimate of the neglected correlation effects. According to Slater and Kirkwood,<sup>8,9</sup> the magnitude of this dispersion attraction for species  $a$  and  $b$  at fixed distance is proportional to

$$\frac{\alpha_a \alpha_b}{(\alpha_a/n_a)^{1/2} + (\alpha_b/n_b)^{1/2}}, \quad (4.1)$$

where the  $\alpha$ 's stand for static polarizabilities, and the  $n$ 's are the number of outer-shell electrons.

Table III shows the  $\alpha$ 's and  $n$ 's for the noble gases and for the water molecule. From its entries, and the known empirical Lennard-Jones 12-6 potentials for the pure noble gases,<sup>10</sup> we can estimate the Ne-H<sub>2</sub>O and Ar-H<sub>2</sub>O dispersion attractions through Eq. (4.1). In the minimum energy configuration previously found for the Ne-H<sub>2</sub>O pair ( $R = 3.63 \text{ \AA}$ ,  $\theta = \pm 53^\circ$ ,  $\varphi = 0$ ), we thus estimate an extra dispersion stabilization of

$$-0.135 \text{ kcal/mole}, \quad (4.2)$$

while the analogous extra dispersion stabilization for Ar-H<sub>2</sub>O ( $R = 4.45 \text{ \AA}$ ,  $\theta = \pm 53^\circ$ ,  $\varphi = 0$ ) is found to be

$$-0.174 \text{ kcal/mole}. \quad (4.3)$$

Although the dispersion interaction will tend to depress the potential energy curves somewhat around the distance at which minima occur, and may indeed move the minima inward slightly, it should have little variation with angles  $\theta$  and  $\varphi$ .<sup>11</sup> Under no circumstance is there any reason to believe that the positions of the local minima exhibited for Ne-H<sub>2</sub>O in Fig. 5 would be significantly disturbed upon restoring full electron correlation to the calculation.

In spite of its inadequacy to describe dispersion forces, the Hartree-Fock approximation does admit static polarization. For that reason it is instructive to compare the interaction energies reported in the preceding Section with the classical electrostatic energy of interaction between a point dipole (with moment  $\mu$ ) and a polarizable point particle (polarizability  $\alpha$ ):

$$-(3 \cos^2 \gamma + 1) \alpha \mu^2 / 2R^6. \quad (4.4)$$

TABLE III. Polarizabilities ( $\alpha$ ) and numbers of outer-shell electrons ( $n$ ) for the noble gases<sup>a</sup> and water.<sup>b</sup>

Species	$\alpha(10^{-24} \text{ cm}^3)$	$n$
He	0.20	2
Ne	0.39	8
Ar	1.63	8
Kr	2.46	8
Xe	4.00	8
H <sub>2</sub> O	1.444	8

<sup>a</sup> Noble gas polarizabilities have been taken from *Handbook of Physics*, edited by E. U. Condon and H. Odishaw (McGraw-Hill, New York, 1967), 2nd ed., pp. 7-40.

<sup>b</sup> The isotropic average polarizability for the water molecule has been utilized here, as inferred from optical refractive index measurements; see: D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford U.P., New York, 1969), p.16.

Here  $\gamma$  is the angle between the dipole direction and the vector connecting the particle centers, and  $R$  as before is the relevant distance.

The dipole moment predicted for the water molecule with the present basis set is 2.19 D (experimental value: 1.83 D). Using this value for  $\mu$ , and the Ne and Ar polarizabilities in Table III, we find that Eq. (4.4) predicts energies for Ne-H<sub>2</sub>O, and Ar-H<sub>2</sub>O of -0.0123 kcal/mole and -0.0151 kcal/mole, respectively, for the minimum energy positions previously found along the OH bond directions. Obviously the greater binding that was found for Ne cannot be explained in simple electrostatic terms; some degree of covalency is evidently involved as it is in formation of the more conventional hydrogen bonds. Possibly very slight covalency is also involved in the Ar-H<sub>2</sub>O complex, though the case is less clear. These conclusions bear out the Mulliken population shifts shown in Fig. 7.

The minimum for expression (4.4) as  $\gamma$  varies is achieved at  $\gamma=0^\circ$  and  $180^\circ$ , that is when the dipole points directly toward or away from the polarizable point. The potential minima shown in Fig. 5 along the OH directions hence cannot even qualitatively be explained by interaction (4.4). It should be noted in anticipation of future work that the greater relative importance of interaction (4.4) for Ar-H<sub>2</sub>O might shift potential minima away from the OH directions for that pair.

The hydrogen fluoride-neon pair seems by hindsight to be a good candidate for another weak hydrogen bond. Again the Hartree-Fock approximation should prove to be an effective tool for investigating its existence. Since other hydrogen bonds involving HF tend to be stronger than their analogs with H<sub>2</sub>O replacing HF, the hypothetical FH...Ne bond may well be stronger than the one we have uncovered.

One would not expect to find H<sub>2</sub>O-Ne hydrogen bonds in aqueous solutions of this noble gas. The hydrogen bonds that can and do form between the water molecules themselves are so much stronger, that they alone would preferentially exist in the solution. Instead, one would have to turn for con-

firmation of the present work to an experimental technique such as the molecular beam electric resonance method, which has already proven valuable in the study of hydrogen bonding in small molecular complexes.<sup>12</sup>

\*The portion of this work carried out at N.Y.U. was partly supported by National Science Foundation Grant GP-10331.

<sup>1</sup>For some recent examples, see: (a) P. A. Kollman and L. C. Allen, *Chem. Rev.* **72**, 283 (1972); (b) S. N. Vinogradov and R. H. Linnell, *Hydrogen Bonding* (Van Nostrand, New York, 1971); (c) G. C. Pimentel and A. L. McClellan, *Ann. Rev. Phys. Chem.* **22**, 347 (1971).

<sup>2</sup>(a) N. Bartlett, *Endeavour* **31** (114), 107 (1972); (b) *Gmelins Handbuch der Anorganischen Chemie, Band 1. Edelgasverbindungen*, edited by H.-G. Horn and H. Hein (Verlag Chemie, Berlin, 1970).

<sup>3</sup>(a) K. Morokuma and L. Pederson, *J. Chem. Phys.* **48**, 3275 (1968); (b) P. A. Kollman and L. C. Allen, *J. Chem. Phys.* **51**, 3286 (1969); (c) G. H. F. Diercksen, *Theor. Chim. Acta* **21**, 335 (1971); (d) M. D. Newton and S. Ehrenson, *J. Am. Chem. Soc.* **93**, 4971 (1971); (e) J. E. DelBene, *J. Chem. Phys.* **55**, 4633 (1971); (f) E. Clementi and H. Popkie, *J. Chem. Phys.* **57**, 1077 (1972).

<sup>4</sup>D. Hankins, J. W. Moskowitz, and F. H. Stillinger, *J. Chem. Phys.* **53**, 4544 (1970).

<sup>5</sup>F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **57**, 1281 (1972).

<sup>6</sup>D. B. Neumann, H. Basch, R. L. Kornegay, L. C. Snyder, J. W. Moskowitz, C. Hornback, and S. P. Liebmann, "The POLYATOM (Version 2) System of Programs for Quantitative Theoretical Chemistry" QCPE, University of Indiana, Bloomington, IN.

<sup>7</sup>The ground-state energy quoted in Ref. 4 for the water molecule inadvertently included an extra basis function,  $x^2 + y^2 + z^2$  in pre-exponential character. As a result, the monomer energy quoted there was lower than that in Eq. (2.1). See Erratum to Ref. 4 in *J. Chem. Phys.* **59**, 995 (1973).

<sup>8</sup>J. C. Slater and J. G. Kirkwood, *Phys. Rev.* **37**, 682 (1931).

<sup>9</sup>J. G. Kirkwood, *Phys. Z.* **33**, 57 (1932).

<sup>10</sup>J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Liquids and Gases* (Wiley, New York, 1954), p. 1110. For Ne,  $\epsilon = 4.91 \times 10^{-15}$  erg,  $\sigma = 2.749$  Å; for Ar,  $\epsilon = 1.65 \times 10^{-14}$  erg,  $\sigma = 3.405$  Å.

<sup>11</sup>In this connection it should be recalled that the water molecule polarizability tensor displays only modest anisotropy; see: S. P. Liebmann and J. W. Moskowitz, *J. Chem. Phys.* **54**, 3622 (1971).

<sup>12</sup>T. R. Dyke, B. J. Howard, and W. Klemperer, *J. Chem. Phys.* **56**, 2442 (1972).