

Determination of the pair polarizability tensor for the Ne diatom

James W. Kress* and John J. Kozak

Department of Chemistry and Radiation Laboratory, † University of Notre Dame, Notre Dame, Indiana 46556

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The pair polarizability tensor A for the neon diatom Ne_2 has been determined as a function of the Ne-Ne separation using an extended Gaussian basis set and the finite perturbation coupled Hartree-Fock technique. Our results are compared with calculations reported previously on the Ne diatom (the earlier calculations were based on a density functional approach), and are found to differ significantly in the estimate of the anisotropy in the tensor A .

I. SYNOPSIS OF THE CALCULATION

We have determined the pair polarizability tensor for the neon diatom Ne_2 as a function of Ne-Ne separation (R), using a very extended Gaussian basis set and the finite perturbation coupled Hartree-Fock technique.¹ The neon basis set was determined as suggested by Werner and Meyer,² and a perturbing static electric field strength of 0.01 a. u. was used. The neon basis set is given in Table I. Our results for various values of R are tabulated in Table II and displayed in Figs. 1 and 2. We define $A(R)$, the pair polarizability tensor at a given value of R , as

$$A(R) = \begin{vmatrix} a_{||}(R) & 0 & 0 \\ 0 & a_{\perp}(R) & 0 \\ 0 & 0 & a_{\perp}(R) \end{vmatrix} \text{ a. u.}$$

The various entries listed in Table II are then defined as

$$\alpha_{||}^0(R) = a_{||}(R) - 2\alpha_0,$$

$$\alpha_{\perp}^0(R) = a_{\perp}(R) - 2\alpha_0,$$

$$\alpha(R) = \left(\frac{1}{3}\right) [\alpha_{||}^0(R) + 2\alpha_{\perp}^0(R)],$$

$$\beta(R) = \alpha_{||}^0(R) - \alpha_{\perp}^0(R),$$

where $a_{||}$ is the polarizability component parallel to the Ne-Ne axis, a_{\perp} is the perpendicular component, α_0 is the scalar atomic polarizability, and β is a measure of the anisotropy in A . For comparison, we include in Table II and Figs. 1 and 2 some recent results on the neon diatom by Heller *et al.*,³ who used a density functional formalism to calculate the components of the pair polarizability tensor.

It is immediately evident that the most striking and interesting difference between results obtained using the density functional approach and the results obtained in our study is the structure observed in the Hartree-Fock $\beta(R)$ function between $R=3$ and 5 a. u. The quantum-mechanical origin of the structure in the function $\beta(R)$ is not yet clear. It could be attributed, possibly, to a reorganization of the electronic density at the point of substantial overlap of the $n=2$ functions on each atom. Such a density reorganization would account for the absence of a structural effect in $\beta(R)$ in the density func-

tional results since, in the density functional approach, an atomic additive density approximation was used to determine the total density of the diatom; this approximation does not allow for density changes in the dimeric complex. We note that the problems arising from the use of the additive density approximation in the density functional formalism have been discussed recently by Harris and Heller.⁴ These authors point out that, due to the additive density approximation, the Hellman-Feynman theorem is violated. From their analysis, Harris and Heller conclude that "the effect of a change in the external potential on the sum of the atomic densities is still the *sum of the changes due to each density*" (the italics are ours). From this, then, it is clear that the effect of density reorganization due to intermolecular interaction and its manifestation through the polarizability tensor will not be determined in an additive density approximation.

In order to assess the reliability of our basis set we

TABLE I. Neon Gaussian basis set.

Contracted function number	Type	Exponent	Contraction coefficient
1	S	0.147608	1.0
2	S	0.438834	1.0
3	S	1.20660	1.0
4	S	3.20477	1.0
5	S	10.6125	1.0
6	S	28.8196	1.0
7	S	82.1412	0.213976
	S	255.327	0.071212
	S	907.395	0.017952
	S	4000.20	0.003467
	S	26700.7	0.000447
8, 9, 10	X, Y, Z	0.158909	1.0
11, 12, 13	X, Y, Z	0.397272	1.0
14, 15, 16	X, Y, Z	1.14774	1.0
17, 18, 19	X, Y, Z	3.69786	1.0
20, 21, 22	X, Y, Z	12.5012	0.10692
	X, Y, Z	55.0305	0.016995
23, 24, 25	XX, XY, XZ	0.166667	1.0
26, 27, 28	YY, YZ, ZZ	0.166667	1.0
29, 30, 31	XX, XY, XZ	0.5	1.0
32, 33, 34	YY, YZ, ZZ	0.5	1.0
35, 36, 37	XX, XY, XZ	2.0	1.0
38, 39, 40	YY, YZ, ZZ	2.0	1.0

TABLE II. Neon diatom pair polarizability components.^{a,b}

R	$\alpha(R)$		$\beta(R)$		$\alpha_{ }^0(R)$		$\alpha_{\perp}^0(R)$	
	HF	DF	HF	DP	HF	DF	HF	DF
2.5	-0.2751	...	0.6135	...	0.1339	...	-0.4796	...
3.0	-0.2949	...	0.1838	...	-0.1723	...	-0.3561	...
3.5	-0.1960	...	0.1670	...	-0.0847	...	-0.2517	...
4.0	-0.1104	-0.2023	0.1962	0.3562	0.0204	0.0352	-0.1758	-0.3210
4.5	-0.0553	-0.0802	0.2072	0.3041	0.0828	0.1225	-0.1244	-0.1816
5.0	-0.0247	-0.0286	0.1962	0.2480	0.1062	0.1367	-0.0901	-0.1113
5.5	-0.0095	-0.0086	0.1730	0.1954	0.1058	0.1217	-0.0672	-0.0737
6.0	-0.0027	-0.0010	0.1467	0.1531	0.0951	0.1011	-0.0516	-0.0520
6.5	0.0001	0.0010	0.1219	0.1218	0.0814	0.0822	-0.0405	-0.0396
7.0	0.0010	0.0010	0.1008	0.0978	0.0682	0.0662	-0.0326	-0.0316
8.0	0.0013	0.0004	0.0693	0.0656	0.0475	0.0441	-0.0218	-0.0215
9.0	0.0007	0.0001	0.0483	0.0463	0.0329	0.0310	-0.0154	-0.0153

^aAll entries are in a.u.: 1 a.u. (length) = 0.529167 Å; 1 a.u. (polarizability) = 0.148176 Å³.

^b $\alpha_0 = 2.3698$ a.u.

have, for the field-free system, calculated the Ne-Ne Hartree-Fock potential energy function. The results of these calculations are given in Table III along with the Hartree-Fock limit results of Gilbert and Wahl.⁵ It is evident that the agreement between the two calculations is excellent, thus indicating that spurious polarization effects due to basis-set inadequacy are not present to any significant degree in our calculation.

To assess the dependability of the fixed-field analysis,

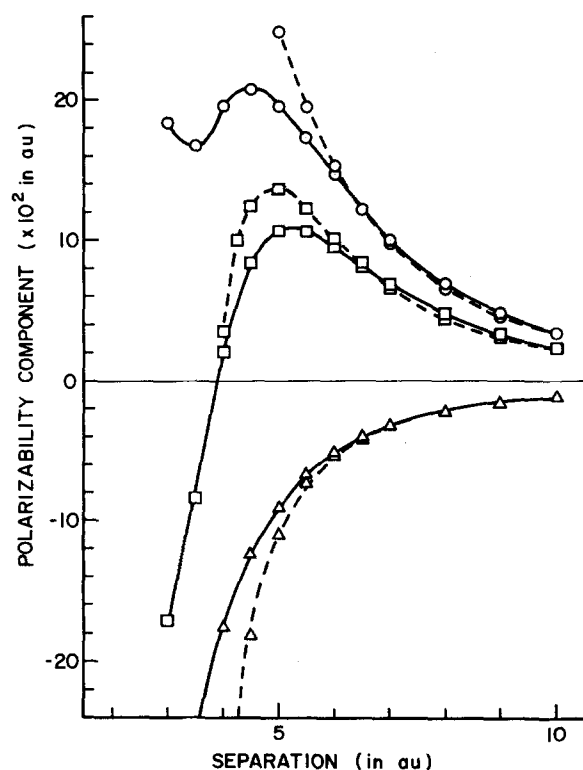


FIG. 1. A plot of the components of the pair polarizability tensor as a function of separation R for the Ne_2 system. The solid lines correspond to the Hartree-Fock results obtained in this work, and the dashed lines represent the density-functional results reported in Ref. 3. In this figure the squares denote $\alpha_{||}^0$, the triangles denote α_{\perp}^0 and the circles denote β .

one may follow the procedure suggested in Ref. 1. Let

$$\mu_q = \mu_q^0 + \sum_{q'} a_{qq'} E_{q'}, \quad (1)$$

where μ is the total dipole moment, μ^0 is the field-free

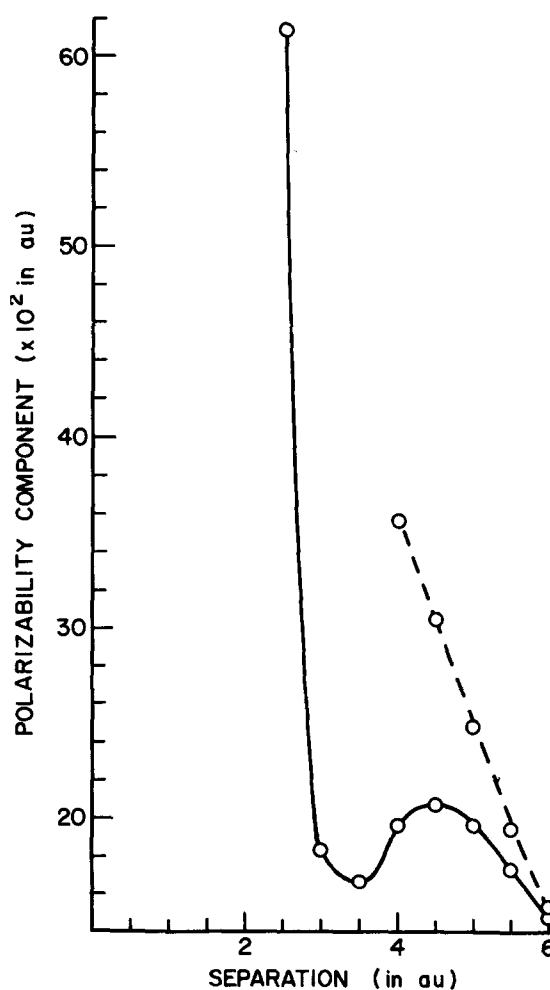


FIG. 2. A plot of β as a function of separation R for the Ne_2 system in the small R regime. The conventions adopted here are the same as those used in Fig. 1.

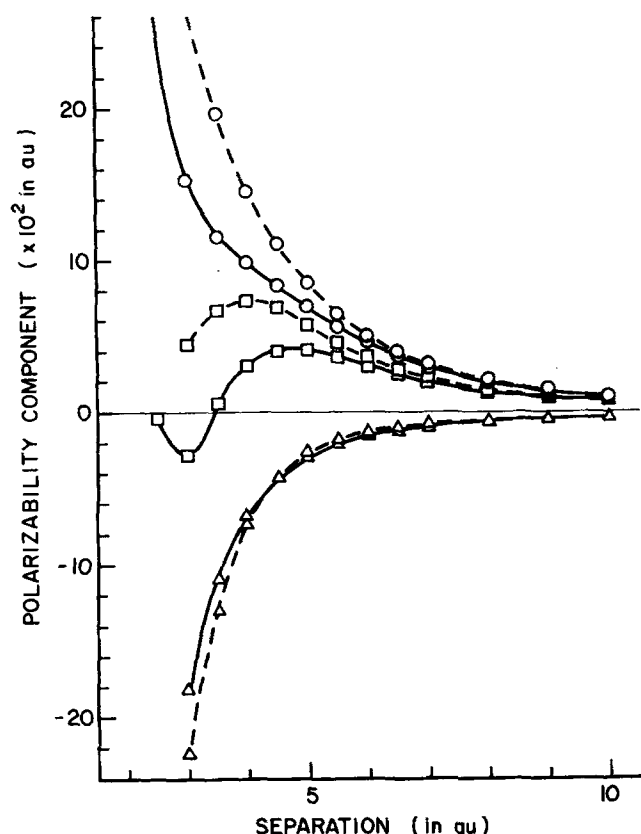


FIG. 3. A plot of the components of the pair polarizability tensor as a function of separation R for the He_2 system. The conventions adopted here are the same as those used in Fig. 1.

From this calculation we again conclude that $E = 0.01$ a. u. results adequately represent the physical phenomena being considered.

In light of the results found in the neon diatom case, we have also re-examined the He_2 system. Our results, along with those reported in several earlier studies,^{3,6,7} are given in Table IV and Fig. 3. In the He case we find no structure in the $\beta(R)$ function. In the interval $3 < R < 5$ a. u. we see a slight inflection in the slope of the function $\beta(R)$ vs R at $R = 4.5$ a. u., but changes of the order of magnitude observed are only slightly larger than the numerical noise and therefore may or may not be significant.

II. CONCLUDING REMARKS

The results obtained in this study raise a number of interesting questions:

(1) Is the structure observed in the function $\beta(R)$ vs R real, or is it an artifact of Hartree-Fock theory which can be removed via a multiconfiguration (CI) calculation?

(2) To what extent is the observed structure in the function $\beta(R)$ of importance as regards determination of the Ne-Ne pair potential? Would the resulting pair

potential be consistent with one determined via a molecular beam experiment?

(3) Might the structure observed in the function $\beta(R)$ affect the macroscopic properties in a significant way, for example, the Clausius-Mossotti function, the dielectric virial coefficients, and the light scattering properties, particularly at high temperature?

(4) Would the structure observed in the function $\beta(R)$ for the neon diatom also appear in a similarly extended calculation on the argon diatom and, if so, would the effect be as pronounced as the one observed for Ne_2 ?

As a concluding remark, several authors have pointed out that, in order to understand fully dielectric phenomena, the role of the molecular polarizability must be considered explicitly.^{8,9} Indeed, it has been suggested that not only the polarizability but also the functional dependence of the polarizability on interparticle separation must be taken into account in order to explain the behavior of the Clausius-Mosotti function with varying density.¹⁰ In a previous contribution, the present authors have analyzed and exhibited the crucial importance of intermolecular polarization contributions to the static dielectric constant of water.⁹ This analysis was carried out by assuming that the polarizability of water was independent of the water-water separation. Given the results reported in this communication the question now arises whether the structure observed in the function $\beta(R)$ for the neon diatom Ne_2 would also be observed in the *isoelectronic* system $(\text{H}_2\text{O})_2$, and if so whether this effect might be important in understanding the static dielectric properties of water. Work is now in progress to attempt to answer these questions, the results of which will be reported in a subsequent contribution.

*Present address: Department of Chemical Engineering, University of Notre Dame, Notre Dame, IN 46556.

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