## Determination of the pair polarizability tensor for the Ne diatom

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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. The neon basis set was determined as suggested by Werner and Meyer, 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

$$A(R) = \begin{vmatrix} a_{11}(R) & 0 & 0 \\ 0 & a_{1}(R) & 0 \\ 0 & 0 & a_{1}(R) \end{vmatrix}$$
 a. u.

The various entries listed in Table II are then defined as

$$\alpha_{11}^{0}(R) = a_{11}(R) - 2\alpha_{0},$$

$$\alpha_{1}^{0}(R) = a_{1}(R) - 2\alpha_{0},$$

$$\alpha(R) = (\frac{1}{3}) \left[\alpha_{11}^{0}(R) + 2\alpha_{1}^{0}(R)\right],$$

$$\beta(R) = \alpha_{11}^{0}(R) - \alpha_{11}^{0}(R),$$

where  $a_{\parallel}$  is the polarizability component parallel to the Ne-Ne axis,  $a_{\perp}$  is the perpendicular component,  $\alpha_0$  is the scalar atomic polarizability, and  $\beta$  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			Contraction
number	Type	Exponent	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. 2,b

	α(1	R)	$\beta(R)$		$\alpha_{\rm H}^{\rm D}(R)$		$\alpha_{\perp}^{0}(I$	R)
R	. HF	DF	HF	DP	HF	DF	HF	$\mathbf{DF}$
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

<sup>&</sup>lt;sup>a</sup>All entries are in a.u.: 1 a.u. (length) = 0.529167 Å; 1 a.u. (polarizability) = 0.148176 Å<sup>3</sup>.

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. <sup>5</sup> 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,

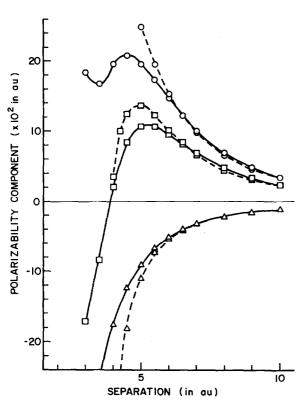


FIG. 1. A plot of the components of the pair polarizability tensor as a function of separation R for the Ne<sub>2</sub> system. The solid lines correspond to the Hartree-Fock results obtained in this work, and the dashed lines represent the density-functional results reported in Ref. 3. In this figure the squares denote  $\alpha_0^0$ , the triangles denote  $\alpha_1^0$  and the circles denote  $\beta$ .

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

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

where  $\mu$  is the total dipole moment,  $\mu^0$  is the field-free

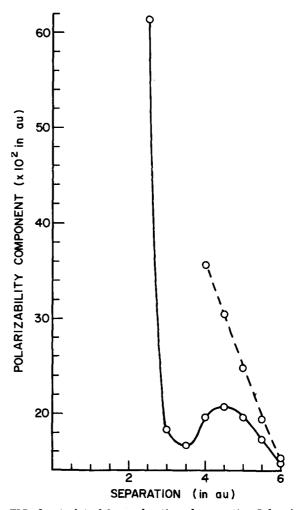


FIG. 2. A plot of  $\beta$  as a function of separation R for the Ne $_2$  system in the small R regime. The conventions adopted here are the same as those used in Fig. 1.

 $<sup>^{</sup>b}\alpha_{0} = 2.3698 \text{ a.u.}$ 

TABLE III. Neon diatom potential curve.

$R^{\mathbf{a}}$	E(GW)a,b	$E(KK)^{c,e}$	$\Delta^{\mathbf{d}}$
2.5	0.3305	0.3243	1.88
3.0	0.0973	0.0960	1.34
3.5	0.0287	0.0285	0.70
4.0	0.0084	0.0084	0
4.5		0.0025	
5.0	0.0007	0.0007	0
5, 5	0.0002	0.0002	0

Entries in atomic units: 1.a.u. (energy)

dipole moment, E is the applied electrostatic field vector, and the subscripts q denote the x, y, or z component. As pointed out by Cohen and Roothaan, the computational technique described in Ref. 1 is exact only in the limit E=0. Our fixed-field results were checked by examining the case E = 0.01 and 0.001 a.u. for a separation R equal to 3.5 a.u. [the position of the minimum in the  $\beta(R)$  curve for Ne<sub>2</sub>]; these calculations were designed to maximize the precision in our numerical work while minimizing the effects due to field strength. Upon extrapolation to E=0, a difference of 0.0011 a.u. in  $a_{\rm ll}$  [the difference being defined as  $a_{qq}(E=0.01) - a_{qq}(E=0.01)$ =0)] and 0.0023 a.u. in  $a_1$  was determined. The difference in  $\beta$ , i.e.,  $\beta(E=0.01) - \beta(E=0)$ , was found to be -0.0012 a.u. From these results we conclude that the results for E = 0.01 a.u. satisfactorily represent the limiting results for E = 0.

More recently, Werner and Meyer<sup>2</sup> have pointed out that a more complete representation of Eq. (1) is

$$\begin{split} \mu_{q} &= \mu_{q}^{0} + \sum_{q'} a_{qq'} E_{q'} + 1/2 \sum_{q'} \sum_{q''} b_{q'q''} E_{q'} E_{q''} \\ &+ 1/6 \sum_{q'} \sum_{q'''} \sum_{q'''} c_{qq'q''q''} E_{q'} E_{q''} E_{q'''} + \dots, \end{split} \tag{2}$$

where the coefficients b and c denote hyperpolarizabilities. The  $\mu_{\mathbf{q}}$  may be calculated for various field strengths, and the coefficients a, b, c then determined. In order to assess further the reliability of our results we have calculated (again at R=3.5 a.u.) the  $\mu_{q}$  for three field strengths  $(E = \sqrt{3} \times 10^{-2}, 10^{-2} \text{ and } 10^{-3} \text{ a. u.})$  and then determined the  $a_{11}$  and  $a_{12}$  (estimates were also obtained for the coefficients b and c but these were reliable only to an order of magnitude, see Ref. 2). This calculation revealed a difference of 0.0008 a.u. in  $a_{11}$ , 0.0020 a.u. in  $a_1$ , and -0.0012 a.u. in  $\beta$  [with the differences defined in a manner analogous to that described following Eq. (1)]. Further, the ratios of the third and fourth terms in Eq. (2) to the second term are no larger than  $10^{-3}$  (with E = 0.01 a.u.), thereby indicating that the hyperpolarizability contributions are of negligible importance at the applied field strength considered.

Helium diatom pair polarizability components TABLE

		$\alpha(R)^a$	<b>a</b> (	ļ.		$\beta(R)^{2}$	oj.			$\alpha_{\rm H}^0(R)^{\rm a}$	R)*			$\alpha_{_{\mathbf{I}}}^0(R)^{\mathbf{a}}$	R)ª	
$R^{2}$	$\mathrm{HF}^{\mathtt{b}}$	HFİ	HF24	$\mathrm{DF}^{\mathfrak{e}}$	HF	HFİ	HF2	DF	HF	HF1	HF2	DF	HF	HF1	HF2	DF
2.5	-0.196	:	:		0.285	:	:	:	- 0, 005	:	:	:	-0.291	:	:	:
3.0	-0,131	:	:	-0.134	0.153	:	:	0.268	-0.029	:	:	0.044	-0.182	:	•	-0.224
3.5	-0.072	:	-0.072	-0.064	0.115	:	0.113	0.196	0.005	:	0.003	0.066	-0.110	:	-0.110	-0.130
4.0	-0.035	:	-0.036	-0.025	0.098	0.105	0.096	0.145	0.030	0.031	0.028	0.072	-0.068	-0.074	-0.068	-0.073
4.5	-0.016	:	-0.014	-0.006	0.083	:	0.078	0.110	0.040	:	0.038	0.067	-0.044	:	-0.040	-0.043
5.0	- 0.007	:	-0.007	0,001	0.069	:	0.065	0.084	0.039	:	0.036	0.056	-0.030	:	-0.029	-0.027
5.5	- 0, 003	-0.002	-0.003	0.003	0.056	0.058	0.051	0.064	0.035	0.037	0.031	0.045	-0.021	-0.021	-0.020	-0.019
6.0	- 0, 001	-0.001	-0.002	0.002	0.045	0.044	0.040	0.049	0.029	0.028	0.025	0.035	-0.016	-0.016	-0.015	-0.014
6.5	0.0	:	:	0.001	0.036	:	:	0.039	0.024	:	:	0.027	-0.013	:	:	-0.012
7.0	0.0	:	-0.001	0.001	0.029	:	0.022	0.031	0.019	:	0.014	0.022	-0.010	:	-0.008	-0.009
8.0	0.0	:	-0.001	0.0	0.019	:	0.007	0.021	0.013	:	0.004	0.014	-0.006	:	-0.003	-0.007
0.6	0.0	:	:	0.0	0.013	:	:	0.014	0,009	:	:	0.010	-0.005	:	: }	-0.005
In atom	In atomic units.								Reference 6.	e 6.						

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<sup>=627.503</sup> kcal/mole.

 $<sup>{}^{</sup>b}E(GW)$  denotes results obtained from Ref. 5.

cE(KK) denotes results obtained in this study.

 $<sup>{}^{</sup>d}\Delta = \{ [E(GW) - E(KK)] / E(GW) \} 100.$ 

<sup>&</sup>lt;sup>e</sup>Total energy for infinite separation is

<sup>-257.068430</sup> a.u.

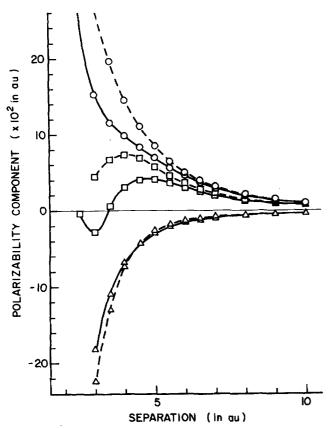


FIG. 3. A plot of the components of the pair polarizability tensor as a function of separation R for the  $\text{He}_2$  system. The conventions adopted here are the same as those used in Fig. 1.

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  $\text{He}_2$  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<sub>2</sub>?

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<sub>2</sub> would also be observed in the isoelectronic system  $(H_2O)_2$ , 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.

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