BRIEF COMMUNICATIONS

ON HARTREE–FOCK DIPOLE POLARIZABILITIES
OF MOLECULES, IONS, AND DEFECTS
IN DUNNING'S BASIS SETS

A. V. Luzanov, A. D. Bochevarov, and O. V. Shishkin   UDC 539.19;548.4

Standard Pople type basis sets generally used to solve applied problems are not quite suitable for *ab initio* calculations of molecular polarizabilities. Even extended basis sets including diffuse AO such as 6-311++G(d, p) lead to understated dipole polarizabilities α. Previously, better AO basis sets were proposed for polarizability calculations. Among these, Sadley's basis [1, 2] proved to be the best one, as demonstrated by α calculations for benzene [3] and a number of DNA nitrous bases [4]. Miscellaneous more complex basis sets were also discussed [5-9].

Here we analyze Dunning's bases, which are not less fundamental than Pople's bases, in the form of correlated basis sets with a diffuse part aug-cc-pvNz [10, 11]. Various examples are used to verify that these bases are applicable to rough estimations of α, easily obtained for medium-sized molecules with standard programs such as GAMESS or GAUSSIAN. Our calculations generally use molecular geometry optimized with the same quantum-chemical scheme with which further polarizability calculations were carried out. Any finite-dimensional realization of the self-consistent MO method is traditionally called below Hartree–Fock realization, and the results of full numerical realization of the proper Hartree–Fock theory are called the Hartree–Fock limit. The values of α are given in atomic units (for dipole polarizability, a.u. = $1.48187 \cdot 10^{-31}$ m^3).

Let us compare the Pople and Dunning AO basis sets for the simplest problem — hydrogen atom (Table 1). As would be expected, without diffuse AO ("+" in Pople's and "aug" in Dunning's bases) the polarizabilities are absolutely unsatisfactory. Nevertheless, some recent works reported the α values obtained with rather limited basis sets such as DZP [12].

As can be seen from Table 1, the simplest Dunning basis with diffuse AO, aug-cc-pvdz, gives an acceptable value of dipole polarizability. At the same time, even with diffuse AO Pople's bases failed to give even 90% of the exact α value. It is not accidental therefore that any quantum-chemical calculation of α with a Pople type basis systematically understates the polarizabilities of hydrogen-containing molecules. For example, a Hartree–Fock calculation of H_2O gave $\alpha = 7.18$ in a large basis 6-311++G($2d$, $2p$) and $\alpha = 7.91$ in a smaller basis, aug-cc-pvdz, which is comparable to the Hartree–Fock limit, $\alpha = 8.505$. Below we give the results of calculations for aug-cc-pvNz alone.

Let us turn to typical diatomic molecules (Table 2). For all molecules except O_2, the experimental data are taken from [4]; for O_2, from [13]. The agreement between the experimental and calculated data may be considered satisfactory if we restrict ourselves to 90% accuracy, bearing in mind that the *ab initio* Hartree–Fock methods, unlike the corresponding semiempirical π-shell models [14], generally give underestimated values of α. The 3-zeta basis set aug-cc-pvtz seems to be an adequate basis to approach the Hartree–Fock limit of polarizability for diatomic molecules. For example, for medium polarizability of the HF molecule in this basis we have 94% Hartree–Fock limit (4.96).

Detailed investigation of electron correlation effects was beyond the scope of this study, but note that for the bases used inclusion of correlation effects generally gives better agreement between the calculated and experimental values. For example, for HF, using the standard scheme of perturbation theory MP2 in the aug-cc-pvtz basis leads to $\alpha = 5.43$, which differs from the experimental value by only 3%.

TABLE 1. Polarizability α, Ground State Energy ε_0, Mean Square of the Coordinate $\langle r^2 \rangle$ of Atomic Hydrogen in Various Bases (all values in au)

Basis	No. of AO	ε_0	$\langle r^2 \rangle$	α
6-311 G(d, p)	6	–0.49981	2.991	0.327
6-311++G(d, p)	7	–0.49982	3.006	0.589
6-311++G($2d$, $2p$)	10	–0.49982	3.006	1.957
6-311++G($3df$, $3pd$)	18	–0.49982	3.006	3.770
cc-pvdz	5	–0.49928	2.973	0.628
aug-cc-pvdz	9	–0.49933	3.024	4.294
aug-cc-pvtz	23	–0.49982	3.008	4.476
aug-cc-pvqz	46	–0.49995	3.003	4.496
Full basis		–0.5	3.0	4.5

TABLE 2. Hartree–Fock Transverse (α_1), Longitudinal (α_2), and Median (α) Polarizabilities of Diatomic Molecules in Dunning's Bases

Molecule	aug-cc-pvdz			aug-cc-pvtz			Experiment		
	α_1	α_2	α	α_1	α_2	α	α_1	α_2	α
H_2	4.45	6.63	5.18	4.59	6.36	5.18	4.82	6.94	5.23
O_2	6.94	15.87	9.93	7.39	16.11	10.29	8.30	15.79	10.80
N_2	9.39	14.42	11.06	9.54	14.32	11.13	9.79	16.06	11.88
HF	3.76	5.42	4.31	4.23	5.33	4.67	5.10	6.59	5.60
CO	10.87	14.11	11.95	11.10	14.05	12.09	12.15	15.72	13.34

For large molecules, the 3-zeta basis sets demand great computer resources. Therefore in calculations of organic molecules we restricted ourselves to the double-zeta basis aug-cc-pvdz, which is more practical (Table 3). The experimental data of Table 2 are borrowed from [13] for the first 7 molecules, from [15] for ethylene and butadiene, and from [14] for uracil. For the latter, we used the geometry given in [4]. For the estimated Hartree–Fock polarizabilities, the agreement with experiment is quite acceptable even for systems (e.g., benzene or uracil) for which considerable electron correlation effects would be expected. It seems that correlation effects are compensated in such systems. The MP2 calculated data for uracil [4] also indicate that the correlation effects are rather weak.

As is known, the most difficult objects of quantum-chemical calculations are anions, whose wave functions have very slow-decaying exponential tails of weakly bound electrons. Therefore even multiexponent basis sets give unsatisfactory estimates of the electric properties of anions. Hopefully, basis sets of aug-cc-pvNz level will adequately reproduce the main tendencies of α variation on passing from one system to another or from one physical situation to another. In this context, it is of interest to compare the polarizabilities of simple monoatomic anions in free state and in crystal. At the same time, we consider a number of typical defects in an ionic crystal, in particular, in a LiF system. Below we use a simple but physically meaningful model of ionic crystal in the form of a rigid point lattice [16]. In this approximation, an ion or defect is placed in an electrostatic field of point charges lying at lattice sites. To calculate the matrix elements of the Hamiltonian of the chosen center (composite ion or defect), it suffices to include a few coordination spheres, redefining the constant Madelung term in an appropriate way.

In our calculations, the chosen center was placed at the center of a cube $9/2a$ in length, where a is the lattice constant ($a = 4$ Å for LiF), in such a way that the Hamiltonian explicitly included an electrostatic potential of 728 point charges. Almost the same results were obtained for a cube $5/2a$ in length. The results of calculations are given in Table 4, where defects are also elementary color centers — F- and F'-centers (1 and 2 electrons, respectively, at an anion vacancy), and also U-center (hydride ion instead of the anion). For impurity centers, we use the symbol v_aB for atom or molecule B at an anion vacancy and v_cB for B at a cation vacancy.

Let us first discuss the solution of the one-electron problem for an F-center. Near the anion vacancy, the ionic

TABLE 3. Components and Mean Value of the Tensor of Hartree–Fock Polarizability of Organic Molecules in the aug-cc-pvdz Basis

Molecule	α_1	α_2	α_3	α	α_{exp}
Methane	16.00	16.00	16.00	16.00	17.27
Ethane	26.22	26.22	29.52	27.32	28.70
Acetylene	18.34	18.34	30.91	22.53	22.45
Benzene	45.16	78.49	78.49	67.38	67.00
Cyclopropane	31.71	36.26	36.26	34.74	34.90
Formaldehyde	12.66	18.13	22.88	18.89	17.30
Nitromethane	21.71	30.08	36.40	29.40	32.60
Ethylene	22.31	23.82	36.31	27.48	28.50
Butadiene	36.59	52.24	68.27	52.37	56.70
Uracil	39.50	67.14	87.17	64.70	63.43

TABLE 4. Hartree–Fock Polarizabilities of Defects and Ion Components in LiF Crystal in the Rigid Point Lattice Model (values for isolated particles given in brackets)

System	aug-cc-pvdz	aug-cc-pvtz	aug-cc-pvqz
F-center	24.79	39.14	43.23
F'-center	31.26	57.35	72.20
U-center	14.03	16.90	17.24
v_aH	3.81	3.66	3.63
v_cH	5.39	8.21	10.41
$v_aH_2 \langle 100 \rangle$	4.67	4.64	4.71
	[5.18]	[5.18]	[5.16]
$v_cH_2 \langle 100 \rangle$	8.09	8.82	9.24
v_aNe	1.80	2.16	2.29
	[1.83]	[2.19]	[2.23]
v_cNe	1.87	1.89	2.40
Li^+	—	0.2163	0.1965
		[0.2157]	0.1964
F^-	4.98	6.13	6.91
	[5.62]	[7.09]	[8.22]

lattice creates a rectangular well $2A/a$ in depth for an electron, where A is the Madelung constant (see, e.g., [17]). Therefore the basis of Gaussian functions must work well, although in the class of one-parameter variational functions the best description of the F-center is obtained in the known solution for a spherical rectangular well [16, 18]. We have carried out an additional study (its details will be published elsewhere) and found that superpositions of 9 Gaussian s-AO for the ground state and 9 p-AO for the excited state with the same exponents in the range of 0.05-0.3 give an exact solution to the problem. The total oscillator strength, equal to 1.00007 for the ground state, testifies to the good quality of the estimated wave functions. Therefore all signs are correct for the corresponding rounded-off polarizability of an F-center $\alpha = 45.44$. Note that even simple model calculations [19] led to a reasonable (in the order of magnitude) estimate of 64.1. Comparing the given exact value with the values of Table 4, one can see that starting from the 4-zeta Dunning basis one can speak about qualitative agreement with "strict" theory. The total oscillator strength rule, however, is not satisfied quite exactly, since we obtain 1.0413 instead of 1.0 even in a 5-zeta basis.

The two-electron system of an F'-center is a still more complex problem, which must be solved in more refined approximations. One can assume, however, that in a 4-zeta basis set the basic electronic properties of this color center are roughly reproduced. At the same time, the U-center and the hydrogen atom at an anion vacancy are also well reproduced

in 3-zeta bases, judging from the fast convergence of α values. On the other hand, the electron of the hydrogen atom at a cation vacancy is extremely weakly bound with the proton and, like the F'-center, demands higher-level bases. Indeed, approximating the wave function of an electron at the v_cH center by 12 Gaussian AO, we obtained $\alpha = 30$ to an accuracy of 1%, which is 3 times as high as the best value of Table 4 (aug-cc-pvqz basis). This system as well as the v_cH_2 defect differ in this dependence on the basis from many-electron atoms, e.g., the Ne atom at the same vacancy (Table 4). The differences are readily understood if we take into account that the electrons of the neon atom have an internal power source of localization — the nucleus field, which is one order of magnitude more powerful than the proton field. The hydrogen atoms are therefore especially sensitive to the "destructive" interaction of an electron at a cation vacancy with the surrounding field (roughly speaking, we have a potential step of the same magnitude, $2A/a$, instead of a well). Inclusion of polarization interaction between the impurity and the lattice ions [16, 20] can slightly reduce this destabilization effect.

In the adopted scheme of basis selection, the isolated ions comprising the LiF crystal also have some peculiarities. For the Li^+ ion, the aug-cc-pvNz basis is actually absent, but the problem may be partly solved by simply assigning Dunning's bases of the hydrogen atom to the lithium atom. The resulting $\alpha = 0.195$ obtained in this way in the aug-cc-pvtz basis is close to the known Hartree–Fock limit $\alpha = 0.189$ [21]. Therefore Li^+ is quite adequately represented in senior bases aug-cc-pvNz for H. For the above reasons, in the case of F^-, the aug-cc-pvNz bases of the fluorine atom give a rather rough description of polarizability for this anion, for which the Hartree–Fock limit $\alpha = 10.65$ [22]. Nevertheless, a transition from the free state of ion to the state of ion in crystal is reproduced correctly: in accordance with Fajans' rule, polarizability increases slightly for a cation surrounded by negative charges but significantly for an anion surrounded by positive charges [23]. Note that using Dunning's neon bases for Na^+ or argon basis for K^+ also gives good estimates of α, for example, the 3-zeta basis for Na^+ gives $\alpha = 0.96$ (Hartree–Fock value $\alpha = 0.94$). Accordingly, for K^+, $\alpha = 5.39$, which is also close to the Hartree–Fock limit ($\alpha = 5.32$). Due to this, more complex computations may be carried out in a single system of basis functions.

Summing up, one can state that even at the Hartree–Fock level standard 2- and 3-zeta basis sets aug-cc-pvdz and aug-cc-pvtz generally give reasonable estimates of molecular polarizability with a mean error of 10%. Electron defects in ion crystals such as color centers as well as anions demand considerably expanded multiexponent basis sets. It is recommended to redefine the exponents of a set of diffuse AO or alter the basis set itself based on analysis of the corresponding problems for electron centers in their initial quantum mechanical formulation.

REFERENCES

1. A. J. Sadley, *Collect. Czech. Chem. Commun.*, **53**, 1995-2016 (1988).
2. G. H. F. Dierckson, V. Kello, and A. J. Sadley, *J. Chem. Phys.*, **79**, 2918 (1983).
3. P. Lazzeretti, M. Malagoli, L. Turci, and R. Zanazi, *ibid.*, **99**, No. 8, 6027-6030 (1993).
4. R. C. Johnson, T. D. Power, J. S. Holt, et al., *ibid.*, **100**, 18875-18881 (1996).
5. V. V. Rossikhin and V. P. Morozov, *Potential Constants and Electrooptic Parameters of Molecules* [in Russian], Énergoizdat, Moscow (1983).
6. J. Almlof and P. R. Taylor, *J. Chem. Phys.*, **92**, 551 (1990).
7. Yu. Luo, H. Agren, O. Vantras, et al., *ibid.*, **98**, No. 9, 7159-7164 (1993).
8. A. V. Bolotin, V. V. Kuzmenko, V. V. Rossikhin, and E. O. Voronkov, *J. Mol. Struct. (Theochem)*, **311**, 233-240 (1994).
9. J. Guan, P. Duffy, J. T. Carter, et al., *J. Chem. Phys.*, **98**, 4753-4765 (1993).
10. T. H. Dunning, *ibid.*, **90**, No. 9, 7159-7164 (1989).
11. R. A. Kendall, T. H. Dunning, and R. J. Harrison, *ibid.*, **96**, 6796 (1992).
12. S. Pal and A. K. Chandra, *ibid.*, **99**, 13895-13867 (1995).
13. S. G. Wulfson, *Molecular Magnetochemistry* [in Russian], Nauka, Moscow (1991).
14. Yu. F. Pedash, V. F. Pedash, and A. V. Luzanov, *Zh. Strukt. Khim.*, **27**, No. 1, 164-166 (1986).
15. D. S. Chemla and J. Zyss (eds.), *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press, Orlando (1991).
16. A. M. Stoneham, *Theory of Defects in Solids*, Clarendon Press, Oxford (1975).
17. I. V. Abarenkov, *Vestn. Leningr. Univ.*, No. 16, 5-13 (1958).

18. *Color Centers in Alkali Halide Crystals* [in Russian], IL, Moscow (1958).

19. M. N. Adamov, M. N. Ledovskaya, and T. K. Rebane, *Vestn. Leningr. Univ.*, No. 4, 28-31 (1967).

20. G. M. Zhidomirov, A. L. Schluger, and L. N. Kantorovich, in: *Modern Problems in Quantum Chemistry: Quantum-Chemical Methods in Theory of Intermolecular Interactions and Solids* [in Russian], Nauka, Leningrad (1987), pp. 224-281.

21. H. Coker, *J. Phys. Chem.*, **80**, No. 19, 2078-2084 (1976).

22. S. Wilson, *Electron Correlation in Molecules*, Clarendon Press, Oxford (1984).

23. V. S. Urusov, *Theoretical Crystal Chemistry* [in Russian], Moscow State University, Moscow (1987).