Dipole Moments, Polarizabilities, and Infrared Intensities Calculated with Electric Field Dependent Functions

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Electrical properties of molecules are difficult to compute accurately, and traditional calculations typically require large basis sets with multiple sets of diffuse and polarization functions. Ditchfield, Sadlej, and Almlöf have shown that much smaller basis sets can be used if electric dependence is incorporated into the basis set. We have combined the features of these methods and allowed the center of each Gaussian, A, to depend on the field, ϵ, according to $A(\epsilon) = A(0) - \alpha^n \lambda \epsilon$, where α is the Gaussian exponent, n is a fixed integer, and λ is a parameter chosen to maximize the polarizability in a series of reference molecules. The field dependence is used in both the exponential and the preexponential factors in the Gaussian basis functions. Electric field dependent HF/6-31+G** calculations of dipole moments, polarizabilities, and infrared intensities are approximately the same quality as HF/6-311++G(3d,3p) calculations without field dependent functions (the improvement is most striking for the polarizabilities of linear molecules). Field dependence of the outer valence and diffuse functions appears to be the most important. The results for $n = -2$ and $n = 0$ are very similar; the existing codes for geometrical derivatives of the energy can be easily modified to compute improved electrical properties for the $n = 0$ case.

Introduction

The dipole moment vector, μ, the polarizability tensor, α, and the infrared intensities, A, are important molecular properties. They provide information about the distribution of charge within a molecule and how it changes with an applied electrical field and with molecular vibrations. Unfortunately, electrical properties are notoriously difficult to calculate accurately because they depend on the outer parts of the wave function.[1] One approach is to use a very large basis set, augmented with multiple diffusion and polarization functions, to provide more flexibility in the valence region of the wave function (see refs 2–4 for examples). However, such calculations can be quite expensive except for small molecules.

An alternate approach is to use a modest size basis set and to build in some functional dependence on the applied electric field. Three different approaches have been tried previously. Ditchfield[5] used field dependent basis functions of the form

$$\phi = (x - A_x)^{1Ax} (y - A_y)^{1Ay} (z - A_z)^{1Az} \times$$
$$\exp(-\alpha(\mathbf{r} - \mathbf{A})^2) \exp(k\epsilon \cdot (\mathbf{r} - \mathbf{A})) \quad (1)$$

where k is chosen to maximize the molecular polarizability (different k for each shell in the basis). Sadlej[6] used basis functions of the form

$$\phi = (x - A_x)^{1Ax} (y - A_y)^{1Ay} (z - A_z)^{1Az} \times$$
$$\exp(-\alpha(\mathbf{r} - \mathbf{A} + \lambda\epsilon/\alpha^2)^2) \quad (2)$$

where λ is chosen to maximize the molecular polarizability and λ is different for x, y, z directions but the same λ's are used for all Gaussians in the molecule. Both approaches improved the dipole moments and polarizabilities significantly for calculations with small basis sets. Almlöf and co-workers[7] incorporated an electric field dependence into the wave function by variationally optimizing the positions of each contracted basis function in the molecule in the presence and absence of the field. Properties calculated with a smaller basis set (double-ζ with one set of diffuse and polarization functions) were found to be close to the Hartree–

Fock limit. However, some functions occasionally floated an unreasonable distance away from the nuclear centers.[7]

We have tested an approach that combines features of Ditchfield's, Sadlej's, and Almlöf's methods. The center for each Gaussian is chosen to depend on the electric field according to

$$A(\epsilon) = A - \alpha^n \lambda \epsilon \quad (3)$$

where λ is isotropic to maintain rotational invariance but different λ's are used for each shell for flexibility. The field dependent $A(\epsilon)$ is used in the preexponential factors as well as in the exponential part of the Gaussian basis functions

$$\phi = (x - A_x(\epsilon))^{1Ax} (y - A_y(\epsilon))^{1Ay} (z - A_z(\epsilon))^{1Az} \times$$
$$\exp(-\alpha(\mathbf{r} - \mathbf{A}(\epsilon))^2) \quad (4)$$

The field dependent parameters λ are chosen to maximize the atomic polarizabilities computed with the same basis set.

Computational Methodology

The molecular energy, E, can be expanded in terms of the applied electric field, ϵ:

$$E(\epsilon) = E(0) + \sum_\alpha \left(\frac{\partial E(\epsilon)}{\partial \epsilon_\alpha} \right)_{\epsilon_\alpha=0} \epsilon_\alpha +$$
$$\frac{1}{2} \sum_\alpha \sum_\beta \left(\frac{\partial^2 E(\epsilon)}{\partial \epsilon_\alpha \phi \epsilon_\beta} \right)_{\epsilon_\alpha \epsilon_\beta=0} \epsilon_\alpha \epsilon_\beta + \cdots \quad (5)$$

where $E(0)$ is the energy of the molecule in the absence of the field, and ϵ_α and ϵ_β are the Cartesian components of the electric field. The components of the permanent dipole moments and polarizability tensor are

$$\mu_\alpha = -\left(\frac{\partial E(\epsilon)}{\partial \epsilon_\alpha} \right)_{\epsilon_\alpha=0} \quad (6)$$

TABLE 1: Optimal Values of λ for Hydrogen, Fluorine, Oxygen, Carbon, and Nitrogen[a]

	level of theory		α_{xx}	α_{yy}	α_{zz}	α
		Optimal Values for Hydrogen				
H_2	HF/4-31G	$n = 0, \lambda = 0.0$	0.000	0.000	6.510	2.170
	HF/4-31G	$n = 0, \lambda = 0.0806, 6.0802$	4.358	4.358	6.223	4.979
	HF/4-31G	$n = -2, \lambda = 0.0948, 0.1538$	4.370	4.370	6.223	4.988
	HF/6-31G**	$n = 0, \lambda = 0.0$	0.567	0.567	6.433	2.522
	HF/6-31G**	$n = 0, \lambda = 0.00206, 5.8797, 0.3258$	4.383	4.383	6.260	5.008
	HF/6-31G**	$n = -2, \lambda = -0.00849, 0.1529, 0.4079$	4.383	4.383	6.260	5.008
	HF/6-31++G**	$n = 0, \lambda = 0.0$	0.565	0.565	6.684	2.605
	HF/6-31++G**	$n = -2, \lambda = -0.0817, 0.1555, 0.3977, 0.3816$	4.745	4.745	6.473	5.321
	HF/6-311++G(3d,3p)		4.188	4.188	6.361	4.912
	experimental		4.58	4.58	6.38	5.18
		Optimal Values for Fluorine				
HF	HF/4-31G	$n = 0, \lambda = 0.0$	0.629	0.629	3.837	1.698
	HF/4-31G	$n = -2, \lambda = 0.19309, 0.06213, 0.13424$	3.519	3.519	5.288	4.109
	HF/6-31G**	$n = 0, \lambda = 0.0$	1.978	1.978	4.259	2.739
	HF/6-31G**	$n = 0, \lambda = 0.00016, 0.1414, 1.1093, 0.1698$	3.552	3.552	5.159	4.088
	HF/6-31G**	$n = -2, \lambda = 0.1687, 0.1501, 0.1404, 0.0746$	3.575	3.575	5.194	4.115
	HF/6-31+G**	$n = 0, \lambda = 0.0$	2.786	2.786	4.607	3.393
	HF/6-31+G**	$n = 0, \lambda = 0.00016, 0.01336, 0.6513, 13.0526, 0.0191$	4.461	4.461	5.762	4.895
	HF/6-31+G**	$n = -2, \lambda = 0.2131, 0.1320, 0.0944, 0.1490, 0.1604$	4.467	4.467	5.773	4.902
	HF/6-311++G(3d,3p)		3.802	3.802	5.322	4.309
	experimental		5.10	5.10	6.59	5.60
		Optimal Values for Nitrogen				
NH_3	HF/4-31G	$n = 0, \lambda = 0.0$	8.680	8.680	4.210	7.190
	HF/4-31G	$n = -2, \lambda = 0.18311, 0.02950, 0.12019$	11.059	11.059	10.154	11.057
	HF/6-31G**	$n = 0, \lambda = 0.0$	9.462	9.462	5.678	8.201
	HF/6-31G**	$n = 0, \lambda = 0.00041, 0.0133, 2.6852, 0.55053$	11.656	11.656	10.452	11.255
	HF/6-31G**	$n = -2, \lambda = 0.1618, -0.0629, 0.1215, 0.3895$	11.664	11.664	10.443	11.257
	HF/6-31+G**	$n = 0, \lambda = 0.0$	9.792	9.792	9.763	9.783
	HF/6-31+G**	$n = 0, \lambda = 0.000417, 0.01724, 1.9580, 30.4166, 0.4863$	12.755	12.755	13.295	12.935
	HF/6-31+G**	$n = -2, \lambda = 0.1713, -0.0155, 0.0922, 0.1209, 0.3929$	12.749	12.749	13.289	12.929
	HF/6-311++G(3d,3p)		12.031	12.031	12.682	12.248
	experimental		14.28	14.28	15.90	14.82
		Optimal Values for Carbon				
CH_4	HF/4-31G	$n = 0, \lambda = 0.0$	11.687	11.687	11.687	11.687
	HF/4-31G	$n = -2, \lambda = 0.15207, 0.04045, 0.09763$	15.047	15.047	15.047	15.047
	HF/6-31G**	$n = 0, \lambda = 0.0$	12.540	12.540	12.540	12.540
	HF/6-31G**	$n = 0, \lambda = 0.00067, 0.00597, 3.3717, 0.1767$	15.217	15.217	15.217	15.217
	HF/6-31G**	$n = -2, \lambda = 0.1408, -0.0034, 0.0963, 0.1172$	15.219	15.219	15.219	15.219
	HF/6-31+G**	$n = 0, \lambda = 0.0$	13.051	13.051	13.051	13.051
	HF/6-31+G**	$n = 0, \lambda = 0.00067, 0.01556, 2.6704, 94.6372, 0.2133$	15.971	15.971	15.971	15.971
	HF/6-31+G**	$n = -2, \lambda = 0.1524, 0.0053, 0.0779, 0.1807, 0.1271$	15.971	15.971	15.971	15.971
	HF/6-311++G(3d,3p)		15.613	15.613	15.613	15.613
	experimental		17.28	17.28	17.28	17.28
		Optimal Values for Oxygen				
H_2O	HF/4-31G	$n = 0, \lambda = 0.0$	6.572	1.317	4.295	4.061
	HF/4-31G	$n = -2, \lambda = 0.19308, 0.04783, 0.12411$	8.490	6.072	7.430	7.331
	HF/6-31G**	$n = 0, \lambda = 0.0$	7.019	2.928	5.106	5.018
	HF/6-31G**	$n = 0, \lambda = 0.00027, 0.0152, 1.7676, 0.4661$	8.431	6.197	7.420	7.349
	HF/6-31G**	$n = -2, \lambda = 0.1827, 0.0863, 0.1304, 0.2502$	8.429	6.197	7.420	7.349
	HF/6-31+G**	$n = 0, \lambda = 0.0$	7.274	5.277	5.865	6.139
	HF/6-31+G**	$n = 0, \lambda = 0.00026, 0.0164, 1.0540, 23.5294, 0.3170$	9.151	7.890	8.703	8.581
	HF/6-31+G**	$n = -2, \lambda = 0.1889, 0.0860, 0.0868, 0.1676, 0.1507$	9.142	7.882	8.695	8.573
	HF/6-311++G(3d,3p)		8.547	7.403	7.762	7.904
	experimental		10.32	9.55	9.91	9.92

[a] Polarizabilities in au,[3] experimental values quoted in refs 5 and 6. Order of λ's: core, inner and outer valence, diffuse and polarization.

$$\alpha_{\alpha\beta} = -\left(\frac{\partial^2 E(\epsilon)}{\partial\epsilon_\alpha \partial\epsilon_\beta}\right)_{\epsilon_\alpha\epsilon_\beta = 0} \quad (7)$$

In the double harmonic approximation, the infrared intensity of the ith vibrational mode, A_i, is proportional to the square of the change in the dipole moment with the vibration

$$A_i = \frac{N\pi d_i}{3c^2}\left|\frac{\partial\mu}{\phi Q_i}\right|^2 \quad (8)$$

where N is Avogadro's number, d_i is the degeneracy of the ith mode, c is the speed of light, and $\partial\mu/\partial Q_i$ is the derivative of the dipole moment with respect to the normal mode coordinate Q_i.

If the basis functions do not depend on the applied electric field, the dipole moment in the Hartree–Fock, approximation can be calculated as the expectation value of the dipole moment operator.

$$\mu^0 = \langle\sum_i q_i r_4 i\rangle = -\sum_{\mu\nu} P_{\mu\nu}\langle\mu|\mathbf{r}|\nu\rangle + \sum_A^L Z_A R_A \quad (9)$$

where $P_{\mu\nu}$ is the Hartree–Fock density matrix in the absence of an applied field, Z_A are the nuclear charges, and R_A are the nuclear positions. The polarizability is the derivative of the dipole with respect to the field

$$\alpha^0 = -\left(\frac{\partial^2 E}{\partial\epsilon^2}\right) = \left(\frac{\partial\mu}{\partial\epsilon}\right) = -\sum_{\mu\nu} P^\epsilon_{\mu\nu}\langle\mu|\mathbf{r}|\nu\rangle \quad (10)$$

where $P^\epsilon_{\mu\nu}$ is the derivative of the density matrix with respect to the applied field and is obtained by solving the coupled perturbed Hartree–Fock equations (CPHF).[8] The dipole derivative is the

TABLE 2: Sensitivity of the Polarizability to Changes in λ[a]

molecule			$\lambda = \lambda_{opt}$	$\lambda = 0$	$\lambda = 0.5\lambda_{opt}$	$0.75\lambda_{opt}$	$0.9\lambda_{opt}$
			Hydrogen in H_2				
4-31G	$n = -2$	inner	4.988	4.957			
		outer	4.988	2.460	4.356	4.830	4.963
6-31G**	$n = 0$	inner	5.008	5.008			
		outer	5.008	2.523	4.387	4.853	4.984
		polarization	5.008	5.007			
	$n = -2$	inner	5.008	5.008			
		outer	5.008	2.511	4.381	4.850	4.982
		polarization	5.008	5.007			
6-31++G**	$n = -2$	inner	5.762	5.621			
		outer	5.762	5.462	5.687	5.743	5.759
		diffuse	5.762	4.284	5.333	5.625	5.726
		polarization	5.762	5.762			
			Fluorine in HF				
4-31G	$n = -2$	core	4.109	4.108			
		inner	4.109	4.083			
		outer	4.109	2.583	3.727	4.013	4.093
6-31G**	$n = 0$	core	4.088	4.087			
		inner	4.088	4.064			
		outer	4.088	3.226	3.872	4.033	4.079
		polarization	4.088	4.086			
	$n = -2$	core	4.115	4.114			
		inner	4.115	4.064			
		outer	4.115	3.136	3.835	4.027	4.092
		polarization	4.115	4.114			
6-31+G**	$n = 0$	core	4.895	4.895			
		inner	4.895	4.874			
		outer	4.895	4.636	4.831	4.879	4.893
		diffuse	4.895	4.206	4.713	4.845	4.885
		polarization	4.895	4.895			
	$n = -2$	core	4.902	4.901			
		inner	4.902	4.866			
		outer	4.902	4.569	4.819	4.881	4.899
		diffuse	4.902	4.236	4.727	4.854	4.892
		polarization	4.902	4.901			
			Carbon in CH_4				
4-31G	$n = -2$	core	15.047	15.043			
		inner	15.047	15.025			
		outer	15.047	14.513	14.927	15.024	15.047
6-31G**	$n = 0$	core	15.217	15.216			
		inner	15.217	15.217			
		outer	15.217	14.778	15.108	15.190	15.213
		polarization	15.217	15.216			
6-31G**	$n = -2$	core	15.219	15.216			
		inner	15.219	15.219			
		outer	15.219	14.773	15.108	15.191	15.215
		polarization	15.219	15.219			
6-31+G**	$n = 0$	core	15.971	15.970			
		inner	15.971	15.970			
		outer	15.971	15.721	15.909	15.956	15.969
		diffuse	15.971	15.547	15.865	15.945	15.967
		polarization	15.971	15.970			
	$n = -2$	core	15.971	15.967			
		inner	15.971	15.971			
		outer	15.971	15.718	15.910	15.957	15.969
		diffuse	15.971	15.549	15.865	15.944	15.967
		polarization	15.971	15.970			
			Nitrogen in NH_3				
4-31G	$n = -2$	core	11.057	11.054			
		inner	11.057	11.039			
		outer	11.057	9.273	10.607	10.942	11.038
6-31G**	$n = 0$	core	11.255	11.254			
		inner	11.255	11.251			
		outer	11.255	9.793	10.889	11.163	11.240
		polarization	11.255	11.243			
	$n = -2$	core	11.257	11.255			
		inner	11.257	11.252			
		outer	11.257	9.774	10.886	11.164	11.242
		polarization	11.257	11.243			
6-31+G**	$n = 0$	core	12.935	12.934			
		inner	12.935	12.929			
		outer	12.935	12.281	12.772	12.894	12.928
		diffuse	12.935	11.835	12.669	12.873	12.927
		polarization	12.935	12.926			
6-31+G**	$n = -2$	core	12.929	12.926			
		inner	12.929	12.928			
		outer	12.929	12.256	12.772	12.895	12.926
		diffuse	12.929	11.851	12.659	12.861	12.918
		polarization	12.929	12.918			

TABLE 2 (Continued)

molecule			$\lambda = \lambda_{opt}$	$\lambda = 0$	$\lambda = 0.5\lambda_{opt}$	$0.75\lambda_{opt}$	$0.9\lambda_{opt}$
				Oxygen in H_2O			
4-31G	$n = -2$	core	7.331	7.329			
		inner	7.331	7.305			
		outer	7.331	5.586	6.865	7.199	7.301
6-31G**	$n = 0$	core	7.349	7.348			
		inner	7.349	7.342			
		outer	7.349	6.024	7.018	7.267	7.336
		polarization	7.349	7.341			
6-31G**	$n = -2$	core	7.349	7.347			
		inner	7.349	7.337			
		outer	7.349	5.989	7.009	7.264	7.335
		polarization	7.349	7.343			
6-31+G**	$n = 0$	core	8.581	8.581			
		inner	8.581	8.567			
		outer	8.581	8.191	8.484	8.557	8.577
		diffuse	8.581	7.587	8.320	8.509	8.567
		polarization	8.581	8.578			
	$n = -2$	core	8.573	8.571			
		inner	8.573	8.558			
		outer	8.573	8.168	8.495	8.565	8.577
		diffuse	8.573	7.634	8.338	8.514	8.563
		polarization	8.573	8.571			

a Polarizabilities in au.[3]

derivative of the dipole with respect to the positions of the nuclei

$$\left(\frac{\partial\mu}{\partial R}\right)^0 = -\sum_{\mu\nu} [P^R_{\mu\nu} \langle\mu|\mathbf{r}|\nu\rangle + P_{\mu\nu} \langle\mu|\mathbf{r}|\nu\rangle^R] + \sum_A^L Z_A \quad (11)$$

where $\langle\mu|\mathbf{r}|\nu\rangle^R$ are the derivatives of the dipole moment integral with respect to the atom positions.

If the basis functions depend on the applied field, the one- and two-electron integrals also depend on the field. Since the electrical properties are defined as derivatives with respect to the applied field, there are additional terms arising from the derivatives of these integrals that contribute to the dipole moment, polarizability, and dipole derivatives:

$$\mu = -\left(\frac{\partial E}{\partial\epsilon}\right) = \mu^0 - \sum_{\mu\nu} \left[P_{\mu\nu}\left(h^\epsilon_{\mu\nu} + \frac{1}{2}\sum_{\lambda\sigma} P_{\lambda\sigma} \langle\mu\nu\|\lambda\sigma\rangle^\epsilon\right) - W_{\mu\nu}S^\epsilon_{\mu\nu}\right] \quad (12)$$

$$\alpha = -\left(\frac{\partial^2 E}{\partial\epsilon^2}\right) = \alpha^0 - \sum_{\mu\nu} \left[P_{\mu\nu}\left(h^{\epsilon\epsilon}_{\mu\nu} + \frac{1}{2}\sum_{\lambda\sigma} P_{\lambda\sigma} \langle\mu\nu\|\lambda\sigma\rangle^{\epsilon\epsilon}\right) + P^\epsilon_{\mu\nu}F^{(\epsilon)}_{\mu\nu} - W_\mu\nu S^{\epsilon\epsilon}_{\mu\nu} - W^\epsilon_{\mu\nu}S^\epsilon_{\mu\nu}\right] \quad (13)$$

$$\left(\frac{\partial\mu}{\partial R}\right) = \left(\frac{\partial\mu}{\partial R}\right)^0 - \sum_{\mu\nu} \left[P_{\mu\nu}\left(h^{\epsilon R}_{\mu\nu} + \frac{1}{2}\sum_{\gamma\sigma} P_{\lambda\sigma} \langle\mu\nu\|\lambda\sigma\rangle^{\epsilon R}\right) + P^R_{\mu\nu}F^{(\epsilon)}_{\mu\nu} - W_{\mu\nu}S^{\epsilon R}_{\mu\nu} - W^R_{\mu\nu}S^\epsilon_{\mu\nu}\right] \quad (14)$$

In the above equations, the superscript 0 indicates the property computed without field dependent functions, $W_{\mu\nu}$ is the Lagrangian, and ϵ and R are derivatives with respect to the field and the nuclei. The Fock matrix derivative, $F^{(\epsilon)}_{\mu\nu}$, is defined as

$$F^{(\epsilon)}_{\mu\nu} = h^\epsilon_{\mu\nu} + \sum_{\lambda\sigma} P_{\mu\nu} \langle\mu\nu\|\lambda\sigma\rangle^\epsilon \quad (15)$$

The derivatives of the density $P^\epsilon_{\mu\nu}$ and $P^R_{\mu\nu}$, the Lagrangian $W^\epsilon_{\mu\nu}$ and $W^R_{\mu\nu}$, and the Fock matrix $F^{(\epsilon)}_{\mu\nu}$ are obtained by solving the CPHF equations.[8] The Gaussian 92 suite of programs[9] has been modified to calculate the necessary integral derivatives with

the scalar Rys-quadrature routines and to assemble the field dependent basis function contributions to the electrical properties.

Results and Discussion

Table 1 lists the optimal values of λ for H, F, C, and O for the 4-31G, 6-31G**, and 6-31+G** basis sets. These were obtained by maximizing the polarizability for H_2, HF, CH_4, H_2O, respectively, using the experimental geometries (the λ's for H in HF, CH_4, and H_2O were fixed at the optimal values obtained for H_2). Comparison with nonfield dependent calculations (i.e. $\lambda = 0$) shows that field dependent functions yield significant improvement in the polarizabilities for all three basis sets. The field dependent HF/6-31+G** results appear to be superior to the conventional calculations with the much larger 6-311++G(3d,-3p) basis set. Most of the improvement is obtained when electric field dependent functions are used for the outer valence and diffuse functions. Very little is gained when the polarization functions are field dependent. The results for $n = 0$ and $n = -2$ are almost identical. The $n = 0$ case is particularly attractive, since the integrals needed are the same as above those used for geometric derivatives, and these can be computed efficiently with any well-optimized energy derivative package.

To gain confidence that the outer and diffusion functions contribute the most to the improvement of the polarizability, calculations were carried out with λ's set at different fractions of the optimal value of λ. Table 2 shows that when λ is changed from its optimal value to zero for either the core, inner valence, or polarization functions, the polarizability changes by less than 1% for all cases. For the outer valence and diffusion functions, the effect is more significant. For the hydrogen molecule computed with the 4-31G basis set, setting $\lambda = 0.0$ for the outer valence function reduces the polarizability by 50%; qualitatively similar results are found for HF, H_2O, and NH_3. With the 6-31+G** basis set, field dependence is more important for the diffuse functions than for the outer valence functions. Setting $\lambda = 0$ for the diffuse function reduces the polarizability by 10–25% for H_2, HF, H_2O, and NH_3. Both of these effects are much smaller for nonpolar molecules such as methane. The polarizability does not seem to be too sensitive to the exact value of λ. A 25% change in λ for all of the calculations produces errors no greater than 2.3%, and a 10% change produces errors no larger than 1%. However, the optimal values for λ are quite different for each basis set on a given atom and are not transferable between basis sets.

Calculated dipole moments, polarizabilities, and IR intensities for H_2, HF, H_2O, NH_3, CH_2, CH_4, CO, CO_2, HCN, C_2H_2, H_2-

TABLE 3: Calculated Dipole Moments, Polarizabilities, and Infrared Intensities[a]

	level of theory		μ	α_{xx}	α_{yy}	α_{zz}	α	IR intensities
H_2	HF/4-31G	$n=0, \lambda=0.0$		0.000	0.000	6.349	2.116	
	HF/4-31G	$n=-2, \lambda=\text{opt}$		4.302	4.302	6.072	4.892	
	HF/6-31G**	$n=0, \lambda=0.0$		0.566	0.566	6.310	2.481	
	HF/6-31G**	$n=0, \lambda=\text{opt}$		4.329	4.329	6.139	4.933	
	HF/6-31G**	$n=-2, \lambda=\text{opt}$		4.329	4.329	6.139	4.933	
	HF/6-31++G**	$n=0, \lambda=0.0$		0.564	0.564	6.558	2.562	
	HF/6-31++G**	$n=-2, \lambda=\text{opt}$		5.424	5.424	6.322	5.724	
	HF/6-311++G(3d,3p)			4.188	4.188	6.361	4.912	
	experimental			4.58	4.58	6.38	5.18	
HF	HF/4-31G	$n=0, \lambda=0.0$	0.900	0.626	0.626	3.900	1.717	79.2
	HF/4-31G	$n=-2, \lambda=\text{opt}$	0.717	3.528	3.528	5.344	4.133	64.6
	HF/6-31G**	$n=0, \lambda=0.0$	0.765	1.976	1.976	4.088	2.680	132.7
	HF/6-31G**	$n=0, \lambda=\text{opt}$	0.729	3.527	3.527	4.993	4.015	115.9
	HF/6-31G**	$n=-2, \lambda=\text{opt}$	0.728	3.549	3.549	5.026	4.042	119.1
	HF/6-31+G**	$n=0, \lambda=0.0$	0.803	2.776	2.776	4.450	3.334	176.5
	HF/6-31+G**	$n=0, \lambda=\text{opt}$	0.754	4.430	4.430	5.611	4.824	163.0
	HF/6-31+G**	$n=-2, \lambda=\text{opt}$	0.750	4.435	4.435	5.622	4.831	165.0
	HF/6-311++G(3d,3p)		0.751	3.802	3.802	5.322	4.309	158.2
	experimental		0.716	5.10	5.10	6.59	5.60	
H_2O	HF/4-31G	$n=0, \lambda=0.0$	0.978	6.588	1.334	3.773	3.898	119.7, 2.8, 49.7
	HF/4-31G	$n=-2, \lambda=\text{opt}$	0.714	8.458	6.047	7.171	7.225	88.4, 0.0, 48.4
	HF/6-31G**	$n=0, \lambda=0.0$	0.845	6.767	2.931	4.903	4.867	104.6, 16.3, 57.9
	HF/6-31G**	$n=0, \lambda=\text{opt}$	0.742	8.178	6.146	7.231	7.184	92.7, 6.0, 60.3
	HF/6-31G**	$n=-2, \lambda=\text{opt}$	0.742	8.176	6.146	7.231	7.184	93.2, 5.8, 59.4
	HF/6-31+G**	$n=0, \lambda=0.0$	0.879	7.078	5.243	5.631	5.984	116.0, 22.0, 92.5
	HF/6-31+G**	$n=0, \lambda=\text{opt}$	0.761	8.936	7.842	8.482	8.420	101.0, 11.7, 95.5
	HF/6-31+G**	$n=-2, \lambda=\text{opt}$	0.758	8.928	7.835	8.474	8.412	101.0, 11.0, 93.6
	HF/6-311++G(3d,3p)		0.777	8.547	7.403	7.762	7.904	93.7, 14.9, 88.6
	experimental		0.724	10.32	9.55	9.91	9.92	
NH_3	HF/4-31G	$n=0, \lambda=0.0$	0.560	7.947	7.947	2.815	6.237	611.3, 88.2, 0.6, 27.4
	HF/4-31G	$n=-2, \lambda=\text{opt}$	0.386	10.938	10.938	9.523	10.466	304.6, 54.3, 1.7, 19.3
	HF/6-31G**	$n=0, \lambda=0.0$	0.723	9.193	9.193	5.504	7.963	217.1, 41.4, 0.1, 1.5
	HF/6-31G**	$n=0, \lambda=\text{opt}$	0.591	11.388	11.388	10.300	11.025	152.9, 33.6, 2.2, 2.8
	HF/6-31G**	$n=-2, \lambda=\text{opt}$	0.592	11.395	11.395	10.291	11.027	153.3, 33.5, 2.2, 3.0
	HF/6-31+G**	$n=0, \lambda=0.0$	0.701	9.491	9.451	9.797	9.593	270.7, 61.9, 0.1, 13.5
	HF/6-31+G**	$n=0, \lambda=\text{opt}$	0.595	12.505	12.505	13.274	12.761	187.4, 38.7, 2.3, 12.3
	HF/6-31+G**	$n=-2, \lambda=\text{opt}$	0.595	12.500	12.500	13.268	12.756	186.7, 38.3, 2.4, 12.0
	HF/6-311++G(3d,3p)		0.622	12.031	12.031	12.682	12.248	180.3, 36.7, 1.3, 11.2
	experimental		0.579	14.28	14.28	15.90	14.82	177.0, 15.6–33.7, 4.9, 3.2
CH_2	HF/4-31G	$n=0, \lambda=0.0$	0.862	13.404	8.543	8.155	10.034	0.4, 73.1, 138.5
	HF/4-31G	$n=-2, \lambda=\text{opt}$	0.720	14.407	11.689	12.796	12.964	0.7, 83.3, 117.3
	HF/6-31G**	$n=0, \lambda=0.0$	0.779	13.550	8.315	9.322	10.396	0.1, 61.8, 120.3
	HF/6-31G**	$n=0, \lambda=\text{opt}$	0.704	14.469	11.745	13.204	13.139	1.6, 65.7, 98.1
	HF/6-31G**	$n=-2, \lambda=\text{opt}$	0.704	14.473	11.738	13.210	13.140	1.6, 65.9, 98.3
	HF/6-31+G**	$n=0, \lambda=0.0$	0.872	14.316	9.459	12.416	12.063	0.1, 79.9, 86.7
	HF/6-31+G**	$n=0, \lambda=\text{opt}$	0.735	15.006	12.526	16.435	14.656	4.8, 74.0, 79.1
	HF/6-31+G**	$n=-2, \lambda=\text{opt}$	0.734	15.030	12.528	16.453	14.670	4.8, 74.4, 79.7
	HF/6-311++G(3d,3p)		0.753	15.793	12.922	15.957	14.891	3.8, 62.3, 65.5
CH_4	HF/4-31G	$n=0, \lambda=0.0$		11.594	11.594	11.594	11.594	61.3, 114.3
	HF/4-31G	$n=-2, \lambda=\text{opt}$		14.939	14.939	14.939	14.939	38.1, 105.3
	HF/6-31G**	$n=0, \lambda=0.0$		12.505	12.505	12.505	12.505	30.7, 118.9
	HF/6-31G**	$n=0, \lambda=\text{opt}$		15.177	15.177	15.177	15.177	25.5, 106.2
	HF/6-31G**	$n=-2, \lambda=\text{opt}$		15.179	15.179	15.179	15.179	25.6, 106.6
	HF/6-31+G**	$n=0, \lambda=0.0$		13.023	13.023	13.023	13.023	36.6, 121.4
	HF/6-31+G**	$n=0, \lambda=\text{opt}$		15.937	15.937	15.937	15.937	28.4, 114.6
	HF/6-31+G**	$n=-2, \lambda=\text{opt}$		15.936	15.936	15.936	15.936	28.3, 115.9
	HF/6-311++G(3d,3p)			15.613	15.613	15.613	15.613	28.3, 113.8
	experimental			17.28	17.28	17.28	17.28	41.4, 71.9
								35.4, 63.8
CO	HF/4-31G	$n=0, \lambda=0.0$	0.236	6.765	6.765	12.226	8.585	138.7
	HF/4-31G	$n=-2, \lambda=\text{opt}$	0.103	9.653	9.653	12.602	10.636	119.1
	HF/6-31G**	$n=0, \lambda=0.0$	0.104	7.749	7.749	11.987	9.162	137.9
	HF/6-31G**	$n=0, \lambda=\text{opt}$	0.084	9.823	9.823	12.762	10.803	128.3
	HF/6-31G**	$n=-2, \lambda=\text{opt}$	0.085	9.821	9.821	12.769	10.803	128.2
	HF/6-31+G**	$n=0, \lambda=0.0$	0.097	9.116	9.116	14.098	10.777	159.6
	HF/6-31+G**	$n=0, \lambda=\text{opt}$	0.096	10.670	10.670	13.909	11.750	147.5
	HF/6-31+G**	$n=-2, \lambda=\text{opt}$	0.095	10.691	10.691	13.913	11.765	146.2
	HF/6-311++G(3d,3p)		0.056	10.860	10.860	14.058	11.926	145.0
	experimental		−0.044	12.15	12.15	15.72	13.34	51.1–65.1
CO_2	HF/4-31G	$n=0, \lambda=0.0$		5.345	5.345	21.621	10.770	135.2, 883.3
	HF/4-31G	$n=-2, \lambda=\text{opt}$		10.421	10.421	22.407	14.417	89.1, 861.9
	HF/6-31G**	$n=0, \lambda=0.0$		7.265	7.265	20.047	11.525	137.8, 988.5
	HF/6-31G**	$n=0, \lambda=\text{opt}$		10.427	10.427	21.290	14.048	113.7, 962.8
	HF/6-31G**	$n=-2, \lambda=\text{opt}$		10.424	10.424	21.300	14.050	114.5, 963.3
	HF/6-31+G**	$n=0, \lambda=0.0$		8.352	8.352	23.016	13.240	138.4, 1102.4
	HF/6-31+G**	$n=0, \lambda=\text{opt}$		10.619	10.619	22.990	14.743	121.8, 1077.3
	HF/6-31+G**	$n=-2, \lambda=\text{opt}$		10.651	10.651	23.014	14.772	122.0, 1073.9
	HF/6-311++G(3d,3p)			11.041	11.041	22.705	14.929	125.1, 1086.4
	experimental			10.5	10.5	25.1	15.4	47.7, 498.6

TABLE 3 (Continued)

	level of theory		μ	α_{xx}	α_{yy}	α_{zz}	α	IR intensities
HCN	HF/4-31G	$n=0, \lambda=0.0$	1.265	6.193	6.193	19.625	10.670	128.0, 13.7, 73.1
	HF/4-31G	$n=-2, \lambda=$ opt	1.228	11.381	11.381	19.596	14.119	90.7, 8.6, 70.0
	HF/6-31G**	$n=0, \lambda=0.0$	1.261	7.528	7.528	19.645	11.567	77.3, 12.3, 66.9
	HF/6-31G**	$n=0, \lambda=$ opt	1.251	11.709	11.709	20.117	14.512	72.3, 10.0, 66.2
	HF/6-31G**	$n=-2, \lambda=$ opt	1.252	11.709	11.709	20.126	14.515	72.4, 9.9, 66.1
	HF/6-31+G**	$n=0, \lambda=0.0$	1.299	9.443	9.443	21.709	13.531	98.3, 12.5, 74.0
	HF/6-31+G**	$n=0, \lambda=$ opt	1.293	12.936	12.936	21.539	15.804	78.6, 11.3, 73.0
	HF/6-31+G**	$n=-2, \lambda=$ opt	1.292	12.942	12.942	21.534	15.806	78.5, 11.2, 72.5
	HF/6-311++G(3d,3p)		1.287	13.021	13.021	21.463	15.835	68.8, 11.0, 71.0
	experimental		1.174	12.96	12.96	26.49	17.50	50.2, 0.2, 59.3
HCCH	HF/4-31G	$n=0, \lambda=0.0$		5.992	5.992	27.281	13.088	265.3, 94.4
	HF/4-31G	$n=-2, \lambda=$ opt		14.038	14.038	27.683	18.587	212.4, 88.4
	HF/6-31G**	$n=0, \lambda=0.0$		7.826	7.826	27.905	14.519	199.7, 91.9
	HF/6-31G**	$n=0, \lambda=$ opt		14.669	14.669	28.428	19.255	197.7, 85.9
	HF/6-31G**	$n=-2, \lambda=$ opt		14.672	14.672	28.435	19.259	198.1, 85.6
	HF/6-31+G**	$n=0, \lambda=0.0$		12.289	12.289	30.612	18.397	269.1, 100.7
	HF/6-31+G**	$n=0, \lambda=$ opt		16.009	16.009	30.420	20.813	227.0, 93.5
	HF/6-31+G**	$n=-2, \lambda=$ opt		16.061	16.061	30.425	20.849	226.9, 92.5
	HF/6-311++G(3d,3p)			18.006	18.006	30.250	22.087	225.1, 96.8
	experimental			19.37	19.37	31.92	23.55	162.2-180.2, 62.5
	experimental			17.28	17.28	34.42	23.01	
H₂CO	HF/4-31G	$n=0, \lambda=0.0$	1.188	11.209	5.181	18.232	11.541	5.9, 19.0, 20.9, 91.1, 22.6, 102.1
	HF/4-31G	$n=-2, \lambda=$ opt	1.034	14.312	10.770	19.252	14.778	10.9, 14.0, 38.7, 70.2, 41.6, 74.9
	HF/6-31G**	$n=0, \lambda=0.0$	1.047	13.090	6.714	17.825	12.543	0.6, 23.0, 10.0, 147.3, 49.1, 133.1
	HF/6-31G**	$n=0, \lambda=$ opt	1.009	14.974	10.948	19.064	14.996	4.2, 20.8, 21.9, 129.2, 60.0, 107.8
	HF/6-31G**	$n=-2, \lambda=$ opt	1.011	14.983	10.947	19.074	15.001	4.3, 20.8, 21.9, 129.1, 60.0, 108.1
	HF/6-31+G**	$n=0, \lambda=0.0$	1.135	13.839	8.412	19.909	14.053	1.9, 19.6, 11.6, 164.3, 55.6, 105.4
	HF/6-31+G**	$n=0, \lambda=$ opt	1.092	16.046	11.997	20.766	16.270	5.2, 20.0, 22.4, 150.0, 66.6, 90.7
	HF/6-31+G**	$n=-2, \lambda=$ opt	1.091	16.054	12.005	20.770	16.276	5.2, 20.0, 22.4, 149.1, 66.9, 91.0
	HF/6-311++G(3d,3p)		1.074	15.630	11.745	20.491	15.955	4.0, 20.7, 19.9, 159.9, 66.4, 95.0
	experimental		0.940	18.63	12.95	18.63	16.74	6.5, 9.9, 9.3-11.2, 58.4-73.9, 75.5, 87.6
C₂H₄	HF/4-31G	$n=0, \lambda=0.0$		18.868	6.448	31.492	18.936	1.0, 131.3, 79.0, 22.6, 44.0
	HF/4-31G	$n=-2, \lambda=$ opt		21.723	16.460	33.008	23.730	0.1, 96.4, 12.5, 27.3, 37.3
	HF/6-31G**	$n=0, \lambda=0.0$		19.838	8.719	32.130	20.229	0.2, 98.8, 7.1, 22.5, 38.5
	HF/6-31G**	$n=0, \lambda=$ opt		22.274	17.123	33.442	24.280	0.0, 92.8, 9.8, 22.9, 33.2
	HF/6-31G**	$n=-2, \lambda=$ opt		22.282	17.126	33.447	24.285	0.0, 93.0, 9.8, 23.0, 33.4
	HF/6-31+G**	$n=0, \lambda=0.0$		19.956	17.516	35.277	24.249	0.4, 141.1, 9.6, 20.4, 32.0
	HF/6-31+G**	$n=0, \lambda=$ opt		23.353	19.907	35.913	26.391	0.0, 118.7, 11.3, 22.0, 27.8
	HF/6-31+G**	$n=-2, \lambda=$ opt		23.377	19.958	35.906	26.414	0.0, 118.6, 11.3, 22.3, 28.3
	HF/6-311++G(3d,3p)			23.258	22.143	35.545	26.982	0.0, 118.1, 12.6, 19.4, 25.5
	experimental			26.04	22.94	36.44	28.47	
CH₃F	HF/4-31G	$n=0, \lambda=0.0$	1.036	10.834	10.834	11.613	11.094	89.4, 2.6, 4.4, 7.8, 17.6, 79.1
	HF/4-31G	$n=-2, \lambda=$ opt	0.791	14.062	14.062	15.797	14.640	100.3, 1.9, 0.4, 14.7, 27.9, 64.9
	HF/6-31G**	$n=0, \lambda=0.0$	0.780	12.602	12.602	11.951	12.385	126.4, 6.2, 2.2, 10.9, 31.2, 119.4
	HF/6-31G**	$n=0, \lambda=$ opt	0.702	14.512	14.512	15.143	14.722	122.8, 6.4, 6.9, 2.4, 35.8, 101.7
	HF/6-31G**	$n=-2, \lambda=$ opt	0.701	14.556	14.556	15.169	14.760	125.1, 6.3, 6.9, 2.5, 36.0, 102.2
	HF/6-31+G**	$n=0, \lambda=0.0$	0.862	13.292	13.292	13.299	13.294	153.0, 6.9, 6.3, 6.3, 38.3, 88.3
	HF/6-31+G**	$n=0, \lambda=$ opt	0.796	15.321	15.321	16.403	15.682	140.6, 6.0, 2.5, 10.1, 39.2, 78.7
	HF/6-31+G**	$n=-2, \lambda=$ opt	0.791	15.329	15.329	16.421	15.693	141.9, 5.9, 2.5, 10.1, 39.5, 79.5
	HF/6-311++G(3d,3p)		0.780	14.914	14.914	15.954	15.261	142.6, 6.2, 2.3, 9.5, 37.8, 81.6
	experimental		0.728	16.92	16.92	19.01	17.62	95.0, 2.6, 0.9, 8.7, 24.7, 61.0
								108.3, 1.7, 3.4, 6.0, 37.4, 37.4
CH₂F₂	HF/4-31G	$n=0, \lambda=0.0$	1.103	11.450	9.947	10.207	10.534	13.5, 118.0, 207.1, 27.2, 32.9, 2.7, 26.5, 39.0
	HF/4-31G	$n=-2, \lambda=$ opt	0.857	15.763	13.547	14.417	14.576	6.4, 93.6, 205.3, 13.5, 11.6, 0.1, 32.3, 24.1
	HF/6-31G**	$n=0, \lambda=0.0$	0.807	12.033	12.477	12.105	12.205	7.0, 136.8, 244.4, 31.5, 53.8, 6.7, 52.9, 73.3
	HF/6-31G**	$n=0, \lambda=$ opt	0.769	14.902	14.065	14.329	14.432	
	HF/6-31G**	$n=-2, \lambda=$ opt	0.768	14.961	14.150	14.399	14.503	6.3, 125.4, 237.6, 25.4, 26.3, 1.3, 57.4, 58.5
	HF/6-31+G**	$n=0, \lambda=0.0$	0.904	14.006	13.368	13.594	13.656	7.8, 143.1, 296.3, 28.4, 38.6, 3.4, 47.8, 43.8
	HF/6-31+G**	$n=-2, \lambda=$ opt	0.854	16.571	15.254	15.670	15.832	
	HF/6-311++G(3d,3p)		0.836	16.082	14.642	15.311	15.345	6.5, 278.6, 131.6, 24.4, 20.8, 0.9, 49.1, 39.3
	experimental							4.8, 89.50, 230.4, 14.4, 10.3, 0.0, 22.4, 42.2

a Dipole mopments in au; polarizabilities in au;[3] infrared intensities in km/mol listed in order of increasing frequency (symmetry forbidden modes not included); experimental data quoted in refs 2–7.

CO, C_2H_4, CH_3F, and CH_2F_2 are listed in Table 3. The geometries are optimized at the basis sets at which the calculations are performed, and the optimal λ values for the atoms were taken from Table 1. For all of the molecules in Table 3, the dipole moments computed with the field dependent 6-31+G** basis are within 0.04 D of the value obtained with the 6-31++G(3d,3p) basis without field dependent functions. Even the field dependent 4-31G calculations are within 0.1 D of the 6-31++G(3d,3p) values.

For the hydrogen molecule, the perpendicular components of the polarizability, α_{xx} and α_{yy}, are zero with 4-31G basis set without electric field dependence. With the nonfield dependent

6-31++G** basis, the polarization functions contribute to the perpendicular components, yielding $\alpha_{xx} = \alpha_{yy} = 0.564$ au versus 5.424 au with electric field dependent functions. With the 6-31++G** basis, the parallel component is well represented without field dependent functions at 6.558 au. With field dependent corrections, the value of 6.322 au for α_{zz} is in better agreement with the basis set 6-311++G(3d,3p) and the experimental value.

Similar trends are found for other linear molecules (HF, CO, CO_2, HCN, and C_2H_2). Field dependent functions change the parallel component very little (0.2–1.4 au at 4-31G) but change the perpendicular components much more (3–8 au at 4-31G).

Increasing the basis set size without field dependence has a large effect on the perpendicular components because of the polarization functions but has only a modest effect on the parallel component. With field dependence functions, increasing the basis set size has relatively little effect on either components. Adding diffuse functions increases the polarizability both with and without polarization functions.

For nonlinear molecules, it is difficult to partition the polarizability into parallel and perpendicular contributions for each bond. However, the behavior of the isotropic polarizability is similar to the linear molecules. Polarizabilities computed with field dependent functions are much less sensitive to basis set size than computations without field dependent functions. Field dependent calculations at the HF/6-31+G** level in most cases are as good as or better than HF/6-311++G(3d,3p) computations without field dependence. Furthermore, there is very little difference (± 0.03 au or less) between $n = -2$ and $n = 0$ in the field dependent calculations.

The improvement in the IR intensities is much less spectacular than for the polarizabilities. Intensities calculated at the 4-31G level, both with and without field dependence, can be significantly in error when compared to the HF/6-311++G(3d,3p) values. In general, using field dependent functions tends to reduce the IR intensity (however, there are a few exceptions). At the HF/6-31+G** level, calculations with field dependent functions almost always yield intensities that are closer to the HF/6-311++G-(3d,3p) values than HF/6-31+G** calculations without field dependence. As with the polarizabilities, $n = 0$ and $n = -2$ give nearly the same results (average differences of less than 1 km/mol). Comparison of IR intensities is not as simple because accurate experimental values of absolute intensities are difficult to obtain. Schaefer[2] and Houk[3] have shown that much of the remaining differences between the Hartree–Fock and the experimental IR intensities are due to electron correlation and that calculations of IR intensities at second-order Møller–Plesset perturbation theory with a small basis set (e.g. MP2/6-31+G*) are able to predict the correct qualitative information about the ordering of the intensities.

Conclusion

As discussed in previous papers, the use of electric field dependent functions can improve the calculated values of electrical properties. The improvements in the polarizabilities are more impressive than the dipole moments and IR intensities, and the largest improvements in the polarizabilities are in the components perpendicular to the bond. Field-dependent HF/6-31+G** calculations are approximately the same quality as HF/6-311++G(3d,3p) calculations without field-dependent functions. The results for $n = -2$ and $n = 0$ are very similar; the latter has the advantage that existing integral derivative routines can be used to compute the extra terms arising from the field-dependent basis functions.

References and Notes

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