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LETTERS

Geometry Optimization with an Infinite Basis Set

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We show that geometries can be optimized directly at a level corresponding to extrapolation to an infinite basis set. Numerical examples demonstrate that geometries obtained with gradients extrapolated to the infinite-basis limit agree well with geometries calculated with much bigger basis sets than those used for the calculation. The method may also be used to calculate reaction paths or classical trajectories directly at the extrapolated infinite-basis limit.

1. Introduction

In a recent paper,[1] we proposed a practical scheme for extrapolating electronic energies calculated with polarized double- and triple-ζ basis to the infinite basis-set limit. Numerical tests showed that polarized-sextuple-ζ accuracy could be obtained for a small fraction of the cost. It was also remarked that one could actually optimize geometries at the extrapolated level because the extrapolated energy is a linear combination of four components whose gradients and Hessians are available in standard electronic structure packages. In the present letter, we give examples showing that the method has been reduced to practice and that it works very well.

The method is designed to eliminate the effect of a finite one-electron basis set for a given treatment of the many-electron correlation problem, e.g., Møller−Plesset second-order perturbation theory (MP2) or the coupled clusters method with single and double excitations (CCSD). In particular, it does not eliminate effects due to incompleteness of the many-electron treatment.

2. Theory

Under the power-law assumption of the previous paper,[1] the basis-set limit for the total energy can be expressed as

$$E_\infty^{\mathrm{tot}} = AE_3^{\mathrm{HF}} - AE_2^{\mathrm{HF}} + BE_3^{\mathrm{HF+cor}} - CE_2^{\mathrm{HF+cor}} \qquad (1)$$

TABLE 1: Optimized Geometry of Water

level	basis set	energy	basis functions	r(HO)	θ(HOH)
MP2	cc-pVDZ	−76.2286665	24	0.965	101.97
	cc-pVTZ	−76.3186575	58	0.959	103.43
	cc-pVQZ	−76.3476395	115	0.958	103.97
	TZ|DZ	−76.3704151		0.957	103.96
CCSD	cc-pVDZ	−76.2382061	24	0.965	102.21
	cc-pVTZ	−76.3245565	58	0.957	103.90
	cc-pVQZ	−76.3508121	115	0.955	104.33
	TZ|DZ	−76.3689266		0.955	104.45

TABLE 2: Optimized Geometry of Ammonia

level	basis set	energy	basis functions	r(HN)	θ(HNH)
MP2	cc-pVDZ	−56.3825050	29	1.024	103.92
	cc-pVTZ	−56.4529923	72	1.011	105.94
	cc-pVQZ	−56.4746549	145	1.010	106.46
	TZ|DZ	−56.4944137		1.007	106.59
CCSD	cc-pVDZ	−56.3984299	29	1.027	104.15
	cc-pVTZ	−56.4655362	72	1.012	105.96
	cc-pVQZ	−56.4835251	145	1.013	106.47
	TZ|DZ	−56.5004849		1.006	106.49

where E_X^{HF} is the Hartree−Fock energy with a correlation-consistent[2] (cc-pVXZ) basis, $E_X^{\mathrm{HF+cor}}$ is the correlated energy, and the constants are given by

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TABLE 3: Optimized Geometry of Hydrogen Peroxide

level	basis set	energy	basis functions	r(OO)	r(OH)	θ(HOO)	dihedral angle
MP2	cc-pVDZ	−151.1705963	38	1.457	0.970	98.79	118.47
	cc-pVTZ	−151.3327818	88	1.450	0.964	99.29	114.36
	cc-pVQZ	−151.3844728	170	1.446	0.963	99.67	112.68
	TZ|DZ	−151.4269390		1.449	0.960	99.54	112.66

$$A = \left(\frac{3^\alpha}{3^\alpha - 2^\alpha} - \frac{3^\beta}{3^\beta - 2^\beta}\right) \quad (2)$$

$$B = \frac{3^\beta}{3^\beta - 2^\beta} \quad (3)$$

$$C = \frac{2^\beta}{3^\beta - 2^\beta} \quad (4)$$

This may be derived from the previous paper by noting that

$$\frac{3^\alpha}{3^\alpha - 2^\alpha} - \frac{3^\beta}{3^\beta - 2^\beta} = \frac{2^\alpha}{3^\alpha - 2^\alpha} - \frac{2^\beta}{3^\beta - 2^\beta} \quad (5)$$

As a consequence of eq 1, the gradient with respect to nuclear coordinates can be expressed as

$$\nabla E_\infty^{\text{tot}} = A\nabla E_3^{\text{HF}} - A\nabla E_2^{\text{HF}} + B\nabla E_3^{\text{HF+cor}} - C\nabla E_2^{\text{HF+cor}} \quad (6)$$

and the Lapacian can be written

$$\nabla^2 E_\infty^{\text{tot}} = A\nabla^2 E_3^{\text{HF}} - A\nabla^2 E_2^{\text{HF}} + B\nabla^2 E_3^{\text{HF+cor}} - C\nabla^2 E_2^{\text{HF+cor}} \quad (7)$$

All standard algorithms for geometry optimization can be written in terms of the quantities in eqs 1, 6, and 7.[3,4] The Hessian is used to accelerate convergence to a stationary point but has no effect on the final geometry. These same quantities may also be used to compute reaction paths[5−8] or to carry out classical trajectory calculations.[9,10]

The theory was implemented using a modular interface between the EF algorithm[11−13] for optimization of stationary points and the correlated-electronic-structure calculation capability of GAUSSIAN94.[14]

3. Results

To illustrate the theory, we optimized the geometries of three molecules, namely, H_2O, NH_3, and H_2O_2. We use Møller−Plesset second-order perturbation theory[15] (MP2) for all three cases and the coupled-cluster approximation with single and double excitations[16] (CCSD) for two of them, for a total of five examples. We use the frozen-core approximation in every case. In each of the five cases, we performed geometry optimization with cc-pVDZ ($X = 2$), cc-pVTZ ($X = 3$), and cc-pVQZ ($X = 4$) basis sets and also by extrapolation to an infinite basis from $X = 2$ and 3. The extrapolated calculations used the values of α and β given in ref 1, in particular $\alpha = 3.4$, $\beta = 2.2$ (for MP2) and $\beta = 2.4$ (for CCSD). The results are given in Tables 1−3. In these tables, bond distances r are in Å and bond angles θ and dihedral angles are in degrees. Energies are in hartrees. The notation TZ|DZ in the tables denotes our extrapolated value based on the cc-pVDZ and cc-pVTZ basis sets.

4. Discussion

The tables show that the method is remarkably successful. The geometrical parameters calculated with the infinite basis-set extrapolations of the cc-pVDZ and cc-pVTZ gradients and Hessians are remarkably close to the cc-pVQZ ones in all five cases. It seems reasonable to assume that the extrapolated geometries are actually closer to the infinite-basis results than are the cc-pVQZ geometries. Even if this is not the case, the tables indicate that the extrapolated results are much closer to the quadruple-ζ values than to the triple-ζ ones, and that alone makes the method very powerful.

We recall that for a given molecule, the computer time for the MP2 and CCSD methods scales as the fourth power of the number of basis functions for large systems.[17] Thus, the extrapolated calculations are about an order of magnitude faster than cc-pVQZ. Perhaps even more significant is that cc-pVQZ calculations are often *prohibitively* difficult. Thus, although we can test the extrapolated method for small systems such as those considered here, the alternate to extrapolated results for larger molecules will usually be unextrapolated cc-pVTZ results, which are much less accurate, as illustrated in Tables 1−3.

5. Conclusions

Because the infinite-basis limit of correlated calculations can be well approximated as a linear combination of results obtained with polarized double- and triple-ζ basis, it is possible to obtain good approximations to infinite basis-set gradients and, therefore, to optimize geometries in the infinite-basis limit. One could also use these infinite-basis gradients for direct dynamics[8−10] calculations.

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References and Notes

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