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Implementation of MP2 Gradient in the Generalized Hybrid Orbital (GHO) Method

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Introduction

We have developed QM/MM methods based on generalized hybrid orbitals (GHO)[1]. The GHO method utilizes sp^3 hybridized orbitals at each boundary atom; one of them participates in the QM calculation and the rest three are used as frozen auxiliary orbitals. Recently, we have formulated the analytical energy derivatives of the Møller-plesset second order perturbation theory (MP2) with the GHO method. MP2 reduces the error in the reaction and atomization energies of the Hartree-Fock (HF) method by almost a factor of 10. It is also important to obtain molecular geometries optimized at MP2 especially when the dispersion forces are not negligible in molecular interactions. We present the implementation of the GHO-MP2 gradient method enabling us to calculate accurate molecular structures.

Theory

The nuclear derivative of the μth coefficient of the ith molecular orbital, $C_{\mu i}$, can be expanded in the unperturbed MOs and auxiliary orbitals, $A_{\mu\alpha}$,

$$C^x_{\mu i} = \sum_m^{MO} C_{\mu m} U^x_{mi} + \sum_\alpha^{aux.} A_{\mu\alpha} R^x_{\alpha i} . \tag{1}$$

$R^x_{\alpha i}$ is obtained from the orthogonalization condition between MOs and auxiliary orbitals. The first derivative of the overlap integrals between auxiliary orbitals and MOs are

$$\frac{\partial}{\partial x} S_{\alpha i} = \sum_{\mu\nu} A_{\mu\alpha} S^x_{\mu\nu} C_{\nu i} + \sum_{\mu\nu} A^x_{\mu\alpha} S_{\mu\nu} C_{\nu i} + \sum_\beta^{aux.} s_{\alpha\beta} R^x_{\beta i} = 0 , \tag{2}$$

where $\mathbf{S}$ is the overlap matrix over the entire atomic orbitals and $\mathbf{s}$ is that over auxiliary orbitals. $R^x_{\alpha i}$ is computed from

$$\mathbf{R}^x = -\mathbf{s}^{-1}\left(\mathbf{A}^+\mathbf{S}^x\mathbf{C} + (\mathbf{A}^x)^+\mathbf{S}\mathbf{C}\right). \tag{3}$$

With the MP2 energy expression,

$$E_{\mathrm{MP2}}(\mathrm{GHO}) = \sum_{ij}^{val.}\sum_{ab}^{vir.} T^{ab}_{ij} (ia \mid jb) , \tag{4}$$

$$T^{ab}_{ij} = \frac{2(ia \mid jb) - (ib \mid ja)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} , \tag{5}$$

the presence of the second term in Eq. (1) leads to the MP2 gradient expression with the GHO correction,

$$
\begin{aligned}
E^x_{\mathrm{MP2}}(\mathrm{GHO}) = E^x_{\mathrm{MP2}} &+ 2\sum_{k}^{d.o.}\sum_{\alpha}^{aux.}\sum_{\mu\nu\rho\sigma} R^x_{\alpha k} A_{\mu\alpha} C_{\nu k} \sum_{ij}^{MO} P^{(2)}_{ij} C_{\rho i} C_{\sigma j} \left\{2(\mu\nu\,|\,\rho\sigma) - (\mu\rho\,|\,\nu\sigma)\right\} \\
&+ 2\sum_{ij}^{d.o.} P^{(2)}_{ij} \sum_{\alpha\beta}^{aux.} R^x_{\alpha i} s_{\alpha\beta}\omega_{\beta j} + 2\sum_{ab}^{vir.} P^{(2)}_{ab} \sum_{\alpha\beta}^{aux.} R^x_{\alpha a} s_{\alpha\beta}\omega_{\beta b} \\
&+ \sum_{a}^{vir.}\sum_{i}^{d.o.} P^{(2)}_{ai} \sum_{\alpha\beta}^{aux.} (R^x_{\alpha a} s_{\alpha\beta}\omega_{\beta i} + R^x_{\alpha i} s_{\alpha\beta}\omega_{\beta a}) \qquad , \qquad (6) \\
&+ \sum_{\alpha}^{aux.}\sum_{\mu\nu\rho\sigma} n_\alpha A^x_{\mu\alpha} A_{\nu\alpha} \sum_{ij}^{MO} P^{(2)}_{ij} C_{\rho i} C_{\sigma j} \left\{2(\mu\nu\,|\,\rho\sigma) - (\mu\rho\,|\,\nu\sigma)\right\} \\
&+ 4\sum_{ij}^{act.}\sum_{ab}^{vir.}\sum_{\alpha}^{aux.} T^{ab}_{ij} \left\{R^x_{\alpha i}(\alpha a\,|\,jb) + R^x_{\alpha a}(i\alpha\,|\,jb)\right\}
\end{aligned}
$$

where E^x_{MP2} is the conventional MP2 gradient,[2] $P^{(2)}_{ij}$, $P^{(2)}_{ab}$ and $P^{(2)}_{ai}$ are second order density corrections,[3] n_α is the occupation number of the αth auxiliary orbital, and $\omega_{\alpha i}$ satisfies the modified Fock equation,

$$
\sum_{\nu} F_{\mu\nu} C_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} + \sum_{\alpha}^{aux.}\sum_{\nu} S_{\mu\nu} A_{\nu\alpha}\omega_{\alpha i} \,. \qquad (7)
$$

Result and Discussion

We choose the C7eq (global minimum) conformation of alanine dipeptide to examine the accuracy of GHO-MP2 in the optimized structure. The optimized bond lengths with the cc-pVDZ basis set are listed in Table I. The numbers in the parentheses are deviations of the GHO-MP2 and GHO-RHF results from the full QM MP2 optimized structure. The MP2-GHO method substantially improves the accuracy in the structure compared with GHO-RHF.

The GHO-MP2 gradient method enables us to perform large-scale calculations retaining the precision of MP2. We plan to present efficient GHO-MP2 implementation on PKA(c-AMP dependent protein kinase). We will also show the timing statistics of the parallel implementation of QM/MM MD with GHO-MP2 gradient.

Table I. Optimized bond lengths (Å) in the QM region of C7eq (basis= cc-pVDZ).

TYPE	Connectivity	MP2	GHO-MP2	GHO-RHF
QM - QM	9C – 10O	1.2313	1.2188 (-0.0125)	1.1928 (-0.0385)
	17NH1 – 9C	1.3653	1.3709 (0.0056)	1.3543 (-0.0110)
	18CT3 – 17NH1	1.4518	1.4481 (-0.0037)	1.4428 (-0.0090)
	19H – 17NH1	1.0210	1.0215 (0.0005)	1.0049 (-0.0161)
	20HA – 18CT3	1.1012	1.0996 (-0.0016)	1.0890 (-0.0122)
	21HA – 18CT3	1.1048	1.1053 (0.0005)	1.0933 (-0.0115)
	22HA – 18CT3	1.0988	1.0990 (0.0002)	1.0870 (-0.0118)
Average Error			**-0.00157**	**-0.01586**
Standard Deviation			**0.00558**	**0.01017**

Reference

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