

# Geminal-based wavefunction theory and its perturbative improvement

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Effective treatment of electron correlation, which is missing in mean-field Hartree–Fock (HF) calculations, has been a major topic in quantum chemistry. Electron correlation can be separated into dynamical and static effects. The static electron correlation is essentially important in calculating molecules with near-degenerate states or describing dissociation processes. The antisymmetric product of strongly-orthogonal geminals (APSG) method [1,2] is an effective theory which can account for static electron correlation. The APSG wavefunction is constructed with the two-electron wavefunction, called geminals, and it fully involves the intra-geminal two-electron correlation. To improve the APSG wavefunction by taking the inter-geminal correlation into account, we have applied the Møller–Plesset type multi-configuration perturbation theory (MP-MCPT) to the APSG wavefunction [3,4]. In this presentation, we report the geminal-based wavefunction theories that we have developed recently.

The APSG wavefunction of a closed- or open-shell system is expressed with two-electron geminals  $\{\psi\}$  and one-electron natural orbitals  $\{\varphi\}$  as follows:

$$\Phi_{\text{APSG}} = \hat{A} \left[ \psi^1(x_1, x_2) \psi^2(x_3, x_4) \cdots \psi^{N_C/2}(x_{N_C-1}, x_{N_C}) \varphi_1(x_{N_C+1}) \cdots \varphi_1(x_{N_C+N_O}) \right]. \quad (1)$$

Here,  $\hat{A}$  is the antisymmetrization operator, and  $N_C$  and  $N_O$  represent the numbers of closed- and open-shell electrons, respectively. We applied the MP-MCPT [3,4] to the reference function of Eq. (1).

Table 1 shows the mean absolute errors of geometrical parameters of 30 open-shell diatomic molecules. The MP-MCPT method improves the results of the equilibrium distance and the dissociation energy and obtains the results as well as the other multi-reference perturbation method.

Table 1. Mean absolute errors of the equilibrium distances  $R_e$ , the harmonic vibrational frequencies  $f$ , and the dissociation energies  $D_0$  from the results of experiments for 30 open-shell diatomic molecules (6-311G(2d,2p)) [4].

Method	$R_e$ [pm]	$f$ [ $\text{cm}^{-1}$ ]	$D_0$ [eV]
UHF	2.7	180	1.95
UMP2	2.1	196	0.60
CASSCF	2.3	108	1.14
MRMP2	1.7	87	0.60
APSG	2.4	126	1.07
MP-MCPT(APSG)	1.5	166	0.65

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