Generalized Møller−Plesset Multiconfiguration Perturbation Theory Applied to an Open-Shell Antisymmetric Product of Strongly Orthogonal Geminals Reference Wave Function

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ABSTRACT: The antisymmetric product of strongly orthogonal geminals (APSG) method is a wave function theory that can effectively treat the static electron correlation. Recently, we proposed the open-shell APSG method using one-electron orbitals for open-shell parts. In this paper, we have extended the perturbation correction to the open-shell APSG calculations through Møller−Plesset-type multiconfiguration perturbation theory (MP-MCPT). Numerical applications demonstrate that the present open-shell MP-MCPT can reasonably reproduce the dissociation energies or equilibrium distances for open-shell systems.

1. INTRODUCTION

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. There are several multiconfiguration methods that can take the static electron correlation into account: the most popular one is the complete active space (CAS) self-consistent field (SCF)[1] method. Although the CASSCF method cannot be straightforwardly applied to large systems, in which the selection of the active space orbitals is not obvious, this difficulty can be overcome by methods based on a density matrix renormalization group[2,3] or the restricted configuration methods, for example, restricted active space SCF,[4] constrained CASSCF,[5] occupation-restricted multiple active space SCF,[6] and generalized active space SCF[7] approaches.

Another approach is based on the philosophy of the valence bond theory, in which the total electronic wave function is represented as the product of electron-pair wave functions called geminals. This approach is deeply related to the concept of classical chemical bonds, i.e., covalent-bond pair and lone pair. In the simplest generalized valence bond[8] method, each geminal is constructed with two orbitals, e.g., bonding and antibonding orbitals. The restriction on the number of orbitals constructing a geminal is relaxed in the antisymmetric products of strongly orthogonal geminals (APSG)[9−11] method. Furthermore, the unrestricted strongly orthogonal singlet-type geminals[12] method extended this method to the unrestricted orbital framework that made the open-shell systems tractable. These methods can efficiently span important configurations for describing static electron correlation. In the previous work, we accelerated the SCF convergence in the APSG method and assessed its performance in closed- and open-shell systems.[11] In open-shell systems, one-electron orbitals are used to describe unpaired electrons as

used in ref 12. However, this treatment occasionally gives inappropriate energy because of the unbalanced description of electron correlations in paired and unpaired electrons. Moreover, it does not take into account the dynamical electron correlation between geminals and between a geminal and an unpaired electron orbital.

In the single-reference framework, the Møller−Plesset (MP) perturbation theory (PT), configuration interaction (CI), and coupled cluster models are frequently used to recover dynamical electron correlation. These single-reference models can precisely estimate the geometries and energies of molecules in stable states without degeneracy, though they occasionally result in the failure for systems apart from equilibrium geometries because of the lack of static electron correlations. Therefore, many groups have combined these models with the multiconfiguration method, for example, CASPT[13] and multireference (MR) MP[14] models. For geminal-based theories, APSG-PT[15,16] and the other type of PT[17] have been proposed. We have also developed simple MP-type multiconfiguration PT (MP-MCPT) and assessed its performance in the closed-shell diatomic molecules.[18]

In this study, we apply the MP-MCPT model to the open-shell APSG wave function. We define the Fockian, which is used in the MP-MCPT calculation, for the open-shell APSG reference function. Its numerical performance is assessed in calculations of open-shell diatomic molecules, with a modified GAMESS program.[19] The organization of this paper is as follows. Section 2 presents the theoretical aspects of the present method after brief reviews of the open-shell APSG wave function and MP-MCPT model. Numerical results are shown in section 3. Finally, we give conclusions in section 4.

2. THEORY

2.1. APSG Method for Open-Shell Systems.
First, we briefly explain the APSG method for open-shell systems.[11] The open-shell APSG wave function is constructed as the antisymmetric product of geminals ψ and one-electron orbitals φ, which are used to describe closed- and open-shell parts, respectively:

$$\Phi_{APSG} = \hat{A}[\psi^1(x_1, x_2)...\psi^{N_C/2}(x_{N_C-1}, x_{N_C})$$
$$\varphi_1(x_{N_C+1})...\varphi_{N_O}(x_{N_C+N_O})] \tag{1}$$

where $\hat{A}$ is the antisymmetrization operator and N_C and N_O represent the numbers of electrons in the closed- and open-shell parts, respectively. The strong orthogonality condition is imposed on geminals in the APSG wave function:

$$\int \psi^I(x_1, x_2)\,\psi^J(x_1, x_3)\,dx_1 = 0 \quad (I \neq J) \tag{2}$$

Arai[20] showed that the strong orthogonality condition is equivalent to the expansion of geminals in variationally optimized mutually exclusive subspace. Therefore, a geminal ψ^I is constructed with the natural orbitals in the subspace I, where each natural orbital belongs to one and only one subspace:

$$\psi^I(x_1, x_2) = \sum_{i\in I} C_i^I\, \varphi_i(r_1)\, \varphi_i(r_2)\, {}^1\vartheta(1, 2) \tag{3}$$

with the antisymmetric spin function of ${}^1\vartheta(1,2)$. Here, we used the symbol φ for the one-electron natural orbital that is the same as the one-electron orbitals for open-shell part in eq 1, because both orbitals are simultaneously optimized under the following orthonormality condition:

$$\int \varphi_i(x_1)\, \varphi_j(x_1)\, dx_1 = \delta_{ij} \tag{4}$$

As a result, the APSG wave function is optimized in two aspects. One is the optimization of the coefficients C in geminal expansion of eq 3 by solving the local Schrödinger equation of each geminal. The other is the optimization of natural orbitals of geminals together with open-shell orbitals under the condition of eq 4. After the optimization, the APSG energy is obtained as

$$E_{APSG} = \langle \Phi_{APSG}|\hat{H}|\Phi_{APSG}\rangle \tag{5}$$

2.2. MP-MCPT Model.
This subsection describes the MP-MCPT for closed-shell systems.[18] In perturbation theories, we first construct the zeroth-order equation of an already-known zeroth-order Hamiltonian $\hat{H}^{(0)}$, with its eigensolutions, $E^{(0)}$ and $|\Phi^{(0)}\rangle$:

$$\hat{H}^{(0)}|\Phi^{(0)}\rangle = E^{(0)}|\Phi^{(0)}\rangle \tag{6}$$

The full Hamiltonian $\hat{H}$ is represented as the sum of the zeroth-order Hamiltonian and the residual perturbation:
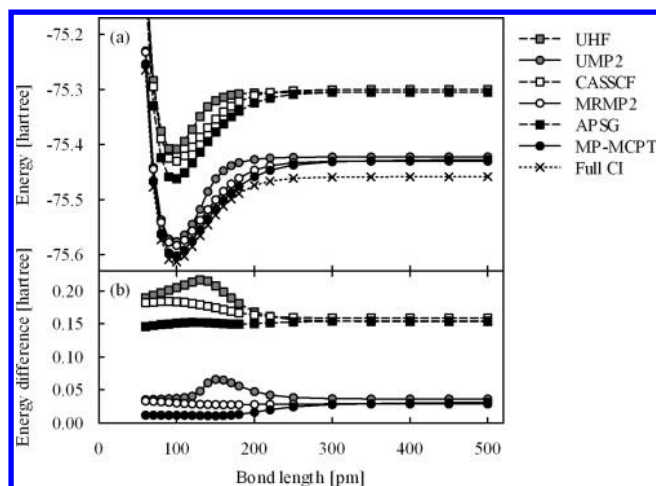
$$\hat{H} = \hat{H}^{(0)} + \hat{W} \tag{7}$$

Then, the energy and the wave function are improved by the perturbation expansion,

$$E = E^{(0)} + E^{(1)} + E^{(2)} + ... \tag{8}$$

$$\Psi = \Phi^{(0)} + \Phi^{(1)} + ... \tag{9}$$

In multireference perturbation theories, the zeroth-order Hamiltonian is occasionally expressed as

$$\hat{H}^{(0)} = E^{(0)}\hat{O} + \hat{P}\hat{F}\hat{P} \tag{10}$$

Figure 1. (a) Potential energy curve for the dissociation of the OH molecule with the 6-311G(d,p) basis set. (b) Energy difference curve from the full CI energy.

where $\hat{O}$ is the operator projecting to the space of the reference function and $\hat{P}$ is the complementary operator of $\hat{O}$.

In MP-MCPT, we distinguish a principal configuration in the reference function $|\Phi^{(0)}\rangle$, denoted by $|HF\rangle$:

$$|\Phi^{(0)}\rangle = c_{HF}|HF\rangle + \sum_{K\in V_R} c_K|K\rangle \tag{11}$$

where V_R is the set of configurations contained in the reference function other than $|HF\rangle$. Note that $|HF\rangle$ may or may not be the lowest-energy configuration. Following the MP perturbation theory for a single determinant reference function, we adopted the single determinant (or HF) density matrix for the Fockian

$$\hat{F} = \sum_{pq}\left(h_{pq} + \sum_i^{occ}\langle pi\|qi\rangle\right)p^+q^- \tag{12}$$

instead of the zeroth-order correlated density matrix. Here, h_{pq} and $\langle pq\|rs\rangle = \langle pq|rs\rangle - \langle pq|sr\rangle$ represent the one-electron and antisymmetrized two-electron integrals, respectively, with $\langle pq|rs\rangle = \int\int \varphi_p^*(x_1)\, \varphi_q^*(x_2)\, r_{12}^{-1}\, \varphi_r(x_1)\, \varphi_s(x_2)\, dx_1\, dx_2$. In eq 12, p, q, ... indicate arbitrary molecular spin orbitals and i limited by "occ" expresses the occupied spin orbital in the main configuration, $|HF\rangle$.

For constructing the first-order correction to the reference wave function, we use the excited configurations from the main configuration, spanned by V_I:

$$|\Phi^{(1)}\rangle = \sum_{K\in V_I} t_K|K\rangle \tag{13}$$

Because this first-order wave function does not satisfy the intermediate normalization condition, we define the following reciprocal vectors for the zeroth-order wave function and excited configurations as

$$\langle \tilde{\Phi}^{(0)}| = \frac{1}{c_{HF}}\langle HF| \tag{14}$$

and

$$\langle \tilde{K}| = \langle K| - \frac{c_K}{c_{HF}}\langle HF| \tag{15}$$
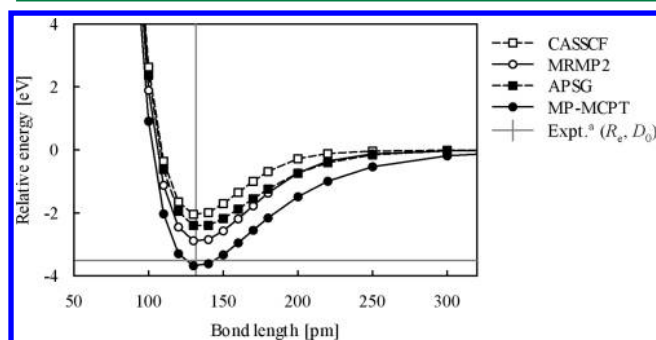
respectively. Using these vectors, the following skew projection operators can be written:

$$\hat{O} = |\Phi^{(0)}\rangle\langle\tilde{\Phi}^{(0)}| \qquad (16)$$

$$\hat{P} = \sum_{K} |K\rangle\langle\tilde{K}| \qquad (17)$$

The sum of the zeroth- and first-order energies is represented as

$$E^{(0)} + E^{(1)} = \langle\tilde{\Phi}^{(0)}|\hat{H}|\Phi^{(0)}\rangle \qquad (18)$$

Figure 2. Potential energy curve for the dissociation of the NF molecule with the 6-311G(2d) basis set. For each calculation, the standard energy is fixed to the energy at 500 pm. [a]Ref 21.

The coefficients t_K in eq 13 are determined by the first-order equation:

$$\sum_{K \in V_I} \langle L|\hat{F} - E^{(0)}|K\rangle t_K$$
$$= -\langle L|\hat{H}|\Phi^{(0)}\rangle + \frac{c_L}{c_{HF}}\langle HF|\hat{H}|\Phi^{(0)}\rangle \quad (L \in V_I) \qquad (19)$$

where V_I is assumed to be restricted to two-electron excited configurations. Then, the second-order energy obtained from the second-order equation is

$$E^{(2)} = \langle\tilde{\Phi}^{(0)}|\hat{H}|\Phi^{(1)}\rangle = \frac{1}{c_{HF}} \sum_{K \in V_I} \langle HF|\hat{H}|K\rangle t_K \qquad (20)$$

2.3. Extension of MP-MCPT Model to Open-Shell Systems. On the basis of the above theoretical background, we extend the MP-MCPT model to open-shell systems, of which the reference wave functions are constructed by the open-shell APSG method. The APSG wave function is rewritten as

$$|\Phi_{APSG}\rangle = c_{HF}|HF\rangle + \sum_{K \in V_{APSG}} c_K|K\rangle \qquad (21)$$

where V_{APSG} represents the intrageminal excited configurations. Because the geminals are expanded as eq 3, V_{APSG} contains two-, four-, six-, and farther electron excited configurations, in which each pair of electrons occupies the same spatial natural orbital in the corresponding geminal subset. The coefficients

Table 1. Equilibrium Distance R_e of 30 Open-Shell Diatomic Molecules with the 6-311G(2d,2p) Basis Set [pm][a]

molecule	UHF	UMP2	CASSCF	MRMP2	APSG	MP-MCPT	exptl.[b]
BeH	134.2	134.1	133.9	134.0	133.7	133.6	134.3
B$_2$*	145.5	147.4	167.4	160.2	154.6	157.5	159.0
CH	110.6	111.3	110.7	110.4	111.3	111.6	112.0
NH*	102.1	103.0	104.8	104.3	103.0	103.4	103.6
CN	115.0	112.6	115.9	117.6	114.8	118.0	117.2
OH	95.1	96.6	97.3	97.5	96.3	96.9	97.0
LiO	167.1	169.2	167.1	168.6	167.9	168.6	169.5
BO	118.1	121.0	119.4	121.3	118.9	121.2	120.5
NO	111.7	113.7	115.9	116.5	114.3	115.4	115.1
O$_2$*	116.1	123.3	122.0	122.4	116.4	124.4	120.8
BeF	135.3	137.1	135.3	137.1	135.9	136.8	136.1
CF	125.5	127.5	127.2	128.0	128.0	127.6	127.2
NF*	129.5	131.9	132.9	133.7	134.6	133.0	131.7
FO	131.5	133.5	138.3	137.2	141.1	137.9	132.6
NaO	203.2	205.7	203.1	204.7	204.1	204.5	205.0
MgH	173.5	173.0	172.8	173.2	172.0	172.1	173.0
MgF	174.4	176.7	174.4	175.5	174.9	176.4	175.0
AlO	168.1	160.3	158.6	162.1	157.6	162.0	161.8
SiH	151.4	151.6	151.1	150.9	151.4	151.7	152.0
SiC*	175.9	169.7	172.1	174.4	170.0	172.1	182.0
SiF	158.8	161.2	158.8	160.4	160.2	161.0	160.1
PH*	141.1	141.7	141.1	141.2	142.1	142.2	142.2
CP	160.3	151.7	156.3	158.1	154.7	157.7	156.2
PO	144.1	149.7	149.2	150.2	146.9	148.9	147.6
SH	133.0	133.6	135.7	135.6	134.0	134.2	134.1
BS	159.8	160.9	160.6	161.6	159.7	160.8	160.9
NS	153.5	142.2	152.5	152.5	152.0	149.4	149.4
SO*	145.0	150.4	151.7	150.6	144.7	149.6	148.1
SF	158.2	161.9	162.6	164.2	161.6	161.9	160.1
ClO	160.9	159.3	166.6	162.2	168.5	163.8	157.0

[a]The molecules with asterisk are triplet, and the others are doublet. [b]Ref 21.

Table 2. Harmonic Vibrational Frequency f of 30 Open-Shell Diatomic Molecules with the 6-311G(2d,2p) Basis Set $[\text{cm}^{-1}]^a$

molecule	UHF	UMP2	CASSCF	MRMP2	APSG	MP-MCPT	exptl.[b]
BeH	2131	2109	2144	2121	2128	2113	2061
B$_2$*	1421	1351	827	1076	1226	1188	1051
CH	3030	2937	3022	3049	2914	2871	2859
NH*	3513	3395	3144	3191	3336	3275	2398
CN	2003	2875	2184	2033	2258	2259	2069
OH	4058	3832	3670	3678	3808	3739	3738
LiO	879	847	878	862	868	869	852
BO	2106	1941	2033	1889	2058	1906	1886
NO	2203	3514	1882	1819	1934	1943	1904
O$_2$*	1973	1426	1541	1537	1872	1432	1580
BeF	1317	1270	1317	1327	1303	1241	1247
CF	1408	1327	1344	1295	1296	1430	1308
NF*	1264	1178	1104	1096	1025	1471	1141
FO	1212	1429	921	1024	822	572	1029
NaO	533	515	535	524	517	657	526
MgH	1549	1558	1587	1615	1595	1562	1495
MgF	761	734	761	676	757	800	712
AlO	813	547	1147	1035	1183	1033	979
SiH	2129	2090	2142	2132	2078	2189	2042
SiC*	828	892	969	903	1263	949	983
SiF	906	867	909	898	871	878	857
PH*	2479	2407	2482	2445	2348	2216	2365
CP	1018	1252	1263	1178	1311	1454	1240
PO	1433	1114	1195	1156	1245	1386	1233
SH	2818	2732	2559	2554	2649	2663	2712
BS	1268	1218	1246	1188	1160	1377	1180
NS	907	1447	1124	1120	1103	2113	1219
SO*	1320	1098	1031	1092	1256	1341	1149
SF	884	809	759	757	772	693	838[c]
ClO	809	810	674	747	638	900	854

^{a}The molecules with asterisk are triplet, and the others are doublet. ^{b}Ref 21. ^{c}Ref 24.

c in eq 21 can be represented with the geminal coefficients C in eq 3 as

$$c_K = \prod_I C_{i_K(I)}^I \tag{22}$$

where $i_K(I)$ represents the natural orbital of the subset I that is occupied in the configuration K. Note that all configurations in $K \in V_{\text{APSG}}$ have single occupations on all orbitals in the open-shell part.

When applying the MP-MCPT model to the open-shell APSG wave function, we have to define the Fockian in eq 12. In this paper, we followed the unrestricted orbital framework, that is, the Fockian is defined as the simple sum of the Fockian for α- and β-spin orbitals:

$$\hat{F} = \sum_{p_\alpha q_\alpha}^{\alpha} \left(h_{p_\alpha q_\alpha} + \sum_{i_\alpha}^{\text{occ}_\alpha} \langle p_\alpha i_\alpha || q_\alpha i_\alpha \rangle + \sum_{i_\beta}^{\text{occ}_\beta} \langle p_\alpha i_\beta | q_\alpha i_\beta \rangle \right) p_\alpha^+ q_\alpha^-$$
$$+ \sum_{p_\beta q_\beta}^{\beta} \left(h_{p_\beta q_\beta} + \sum_{i_\alpha}^{\text{occ}_\alpha} \langle p_\beta i_\alpha | q_\beta i_\alpha \rangle + \sum_{i_\beta}^{\text{occ}_\beta} \langle p_\beta i_\beta || q_\beta i_\beta \rangle \right) p_\beta^+ q_\beta^- \tag{23}$$

where $p_\sigma, q_\sigma, ...$ and i_σ ($\sigma = \alpha$ or β) indicate σ-spin orbitals and "occ$_\sigma$" means the occupied σ-spin orbitals in the main configuration.

The first-order wave function of the MP-MCPT method is constructed of all two-electron excited configurations from the main configuration. A part of them is contained in V_{APSG} as the intrageminal excited configurations. On the other hand, the remainder contains the intergeminal excited configurations and those between geminals and the open-shell part. These configurations mainly improve the wave function by containing the effects that cannot be incorporated in the APSG reference function of open-shell systems.

3. NUMERICAL ASSESSMENTS

We implemented this method into the GAMESS program[19] and assessed its performance in open-shell diatomic molecules by comparison with the results of unrestricted HF (UHF), unrestricted second-order MP (UMP2), CASSCF, second-order MRMP (MRMP2) referring CASSCF function, APSG, and full CI calculations. In CASSCF calculations, we chose the smallest active space that is enough to describe the dissociation processes. The equilibrium distance R_e is obtained from the potential energy curve up to the order of 0.1 pm, except for the UHF and UMP2 cases, where that is determined with the geometry optimization with the analytical energy gradient. The harmonic vibrational frequency f is calculated through numerical differentiation with three points, R_e and $R_e \pm 0.5$ pm. The dissociation energy D_0 is considered as $E(500 \text{ pm}) - E(R_e)$ with considering the zero point energy in D_0 evaluated with the vibrational frequency.

3.1. Potential Energy Curve for OH Molecule. Figure 1a shows the potential energy curve for the dissociation of the doublet OH molecule with the 6-311G(d,p) basis set.[22] All methods in this figure can qualitatively describe correct

Table 3. Dissociation Energy D_0 of 30 Open-Shell Diatomic Molecules with the 6-311G(2d,2p) Basis Set [eV]^a

molecule	UHF	UMP2	CASSCF	MRMP2	APSG	MP-MCPT	exptl.[b]
BeH	2.04	2.24	2.04	2.60	1.64	1.83	2.03
B_2*	−0.60	0.70	1.20	2.48	5.89	4.10	3.02
CH	2.25	3.10	3.14	3.21	3.62	3.62	3.47
NH*	1.97	2.97	2.51	2.99	3.70	3.91	3.54
CN	3.73	6.67	6.19	7.05	6.96	8.28	7.76
OH	2.67	4.10	3.37	4.03	4.15	4.64	4.39
LiO	1.73	3.35	2.06	3.22	3.03	3.78	3.49
BO	6.71	9.64	6.97	8.03	11.00	9.29	8.28
NO	3.76	7.84	5.20	5.59	5.84	7.20	6.50
O_2*	2.37	6.26	3.78	4.73	2.13	6.22	5.12
BeF	4.92	6.39	5.03	6.31	7.32	8.09	6.26
CF	3.33	5.54	4.81	4.83	4.42	5.69	5.67
NF*	0.70	2.97	1.99	2.84	2.37	3.60	3.50
FO	−0.74	1.94	1.06	1.95	1.20	2.41	2.23
NaO	0.76	2.38	3.99	3.61	2.07	2.73	2.60
MgH	2.86	3.57	1.05	1.55	3.66	3.55	1.34
MgF	3.41	4.86	3.51	5.09	6.75	6.85	4.57
AlO	3.29	5.49	3.38	4.78	7.10	7.22	5.27
SiH	2.11	2.71	2.89	2.83	3.30	3.15	3.06
SiC*	3.18	4.19	3.57	3.83	2.97	4.70	4.64
SiF	4.07	5.90	4.60	7.28	5.09	5.98	5.57
PH*	2.05	2.60	2.28	2.49	3.30	3.26	3.02
CP	3.45	5.12	4.21	4.66	4.54	5.55	5.28
PO	3.14	6.79	4.57	4.92	5.26	6.37	6.15
SH	2.43	3.28	2.90	3.15	3.53	3.63	3.55
BS	4.47	6.28	4.46	5.17	4.95	6.95	6.01
NS	3.23	6.00	3.30	3.79	4.06	5.10	4.80
SO*	2.56	5.69	3.57	4.73	4.34	7.54	5.36
SF	1.19	3.20	2.16	2.88	2.45	3.35	3.30
ClO	0.00	2.06	1.27	2.08	1.50	2.35	2.75

^{a}The molecules with asterisk are triplet, and the others are doublet. ^{b}Ref 21.

dissociation curves, while the restricted HF and MP2 methods will fail. However, it is obvious that the dynamical electron correlation plays an important role in accurately reproducing the full CI result. Figure 1b depicts the energy difference curves from the full CI energy, which clearly shows the nonparallelity error for each method. For UHF and UMP2 curves, there exists a hump around 100−200 pm, which increases the nonparallelity errors for UHF and UMP2 up to 63.0 and 30.6 mhartree, respectively. The present MP-MCPT method accurately reproduces the full CI curve both qualitatively and quantitatively, as well as the MRMP2 method: the nonparallelity errors are 5.4 and 20.3 mhartree, and the energy differences at $R = 100$ pm are 30.3 and 11.6 mhartree for the MRMP2 and MP-MCPT methods, respectively.

3.2. Potential Energy Curve for NF Molecule. Next, we assess the method for the triplet ground state. Figure 2 shows the potential energy curve for the dissociation of the triplet NF molecule with the 6-311G(2d) basis set.[22] Experimental values for R_e and D_0 are depicted with the vertical and horizontal lines, respectively. The APSG method underestimates the dissociation energy of the NF molecule because the open-shell APSG wave function does not take into account the correlation of unpaired electrons. Applying the perturbative correction with the MP-MCPT method fairly improves the result (note that zero-point energy should be added to estimate D_0 from the curve). The CASSCF and MRMP2 methods estimate a smaller dissociation energy than that of the APSG and MP-MCPT methods, respectively, because the CASSCF calculation is performed with

a small active space containing eight active electrons and six active orbitals, yielding 120 configurations. Then, we have to perform a 120-dimensional matrix calculation. Enlarging the active space will improve the result, though it need scarcely be said that it requires higher computational costs. On the other hand, the APSG wave function in this calculation is constructed with seven geminals (two cores, four lone pairs, and one bond) and two open-shell orbitals, yielding 486 configurations in this case. However, the APSG method only requires solving six-dimensional matrix calculations at a maximum. It is clear that the APSG method can effectively extract important configurations for describing static electron correlation, and its MP-MCPT correction works quite well.

3.3. Geometrical Parameters of 30 Open-Shell Diatomic Molecules. Tables 1−3 list the calculated equilibrium distance, harmonic vibrational frequency, and dissociation energy of 30 open-shell diatomic molecules, of which experimental data are given in ref 21. We performed UHF, UMP2, CASSCF, MRMP2, APSG, and MP-MCPT calculations with the 6-311G(2d,2p) basis set.[22,23] The experimental vibrational frequency of the SF molecule was taken from ref 24. Table 4 shows the mean error (ME), the mean absolute error (MAE), and the standard deviation σ from the experimental results.

The MP-MCPT method materially improves the results of equilibrium distance and dissociation energy from the APSG results: the MAE of equilibrium distance becomes 1.5 from 2.4 pm, and that of the dissociation energy becomes 0.65 from

Table 4. Mean Error (ME), Mean Absolute Error (MAE), and Standard Deviation σ of the Equilibrium Distance R_e, the Harmonic Vibrational Frequency f, and the Dissociation Energy D_0 from the Results of Experiments for 30 Open-Shell Diatomic Molecules[a]

method	R_e [pm]			f [cm^{-1}]			D_0 [eV]		
	ME	MAE	σ	ME	MAE	σ	ME	MAE	σ
UHF	−1.4	2.7	3.4	+115	180	245	−1.85	1.95	1.06
UMP2	−1.0	2.1	3.6	+134	196	377	+0.04	0.60	0.83
CASSCF	+0.5	2.3	3.4	+30	108	166	−1.05	1.14	0.66
MRMP2	+0.8	1.7	2.2	+17	87	162	−0.33	0.60	0.61
APSG	−0.5	2.4	3.9	+70	126	201	−0.15	1.07	1.34
MP-MCPT	+0.4	1.5	2.6	+100	166	254	+0.61	0.65	0.75

[a]All calculations are performed with the 6-311G(2d,2p) basis set.

1.07 eV by the perturbation corrections, although the MP-MCPT method overestimates the harmonic vibrational frequency. The standard deviations for equilibrium distance and dissociation energy also become smaller. Furthermore, the MP-MCPT method has almost the same magnitude of errors as the MRMP2 method does with slightly larger dispersion in calculating equilibrium distance or dissociation energy.

4. CONCLUSION

We implemented the MP-MCPT method referring the open-shell APSG wave function into the GAMESS program, and its performance was numerically assessed. We succeeded in describing the dissociation processes more properly using the MP-MCPT method than using the APSG method, because the MP-MCPT method can take into account the electron correlation between geminals and between a geminal and an unpaired electron orbital. Furthermore, it was clarified that the MP-MCPT method improves the results of the equilibrium distance and the dissociation energy and obtains the results as well as the other multireference perturbation method.

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Notes
The authors declare no competing financial interest.

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