

## Multiconfiguration Pair-Density Functional Theory in *OpenMolcas*

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### Multiconfiguration pair-density functional theory

Multiconfiguration pair-density functional theory (MC-PDFT)<sup>1,2</sup> combines the advantages of wave function theory and density functional theory to provide a method for efficient simulation of the electronic structure of strongly correlated systems. Strongly correlated systems are systems for which a single configuration state function does not provide a good zero-order approximation to the electronic wave function; strongly correlated systems are sometimes called inherently multiconfigurational systems, multireference systems, or systems with high static correlation. Prominent examples of inherently multiconfigurational systems are molecules with highly stretched bonds, most excited states, many transition metal complexes, and some main-group molecules like ozone, carbonyl oxides, and many others.

In MC-PDFT the first step is to calculate a multiconfiguration wave function, and in *OpenMolcas*, this wave function may be calculated by CASSCF,<sup>3</sup> RASSCF,<sup>4</sup> GASSCF,<sup>5</sup> CAS-CI,<sup>6</sup> RAS-CI,<sup>6</sup> GAS-CI,<sup>7</sup> stochastic-CASSCF,<sup>8</sup> and DMRG.<sup>9,10,11,12,13</sup> CASSCF, RASSCF, and GASSCF are special cases of the multiconfiguration self-consistent-field (MCSCF) method, and one can use either state-specific<sup>14</sup> SCF or state-averaged<sup>15,16</sup> SCF. The total MC-PDFT energy is expressed as

$$E = V_{nn} + \langle \Psi^{MC} | T | \Psi^{MC} \rangle + V_{ne} + V_C + E_{ot}[\rho, \Pi] \quad (1)$$

where the first term corresponds to the nuclear-nuclear interaction; the second, the third, and the fourth terms, respectively, correspond to the kinetic energy, the nuclear-electron attraction, the classical Coulomb interaction of the electronic charge cloud with itself; and the final term is the on-top energy; in Eq. 1 the kinetic energy and the classical electrostatic energy (nuclear-nuclear repulsion energy, nuclear-electron attraction energy and classical electron-electron Coulomb energy) are directly obtained from the multiconfigurational wave function,  $\Psi$ , while the rest of the electronic energy is calculated from an on-top density functional that is a functional of the electron density  $\rho$  and on-top pair density  $\Pi$  (which represents the probability of finding two electrons on top of each other) of that wave function.

Computationally, eq 1 reduces to

$$E = V_{nn} + 2 \sum_i h_{ii} + 2 \sum_{ij} g_{ijij} + \sum_{vw} h_{vw} D_{vw} + 2 \sum_{ivw} g_{iivw} D_{vw} + \frac{1}{2} \sum_{vwxy} g_{vwxy} D_{vw} D_{xy} + E_{ot}[\rho, \Pi] \quad (2)$$

where  $\mathbf{D}$  is the one-electron density matrix,  $\mathbf{h}$  and  $\mathbf{g}$  contain respectively the one- and two-electron integrals,  $i$  and  $j$  are orbitals that are doubly occupied in all configurations (inactive orbitals), and  $v, w, x$ , and  $y$  are active orbitals. An MC-PDFT calculation involves two steps: (1) calculation of the multiconfiguration wave function and (2) calculation of the on-top density functional energy. Because the post-self-consistent-field step is a calculation based on a density functional, the computational effort for step 2 is generally negligible compared to the cost of step 1, which makes MC-PDFT computationally more affordable than other multireference methods such as those based on perturbation theory or multireference configuration interaction.

MC-PDFT always uses multiconfiguration wave functions that are spin eigenfunctions. MC-PDFT is free from delocalization error,<sup>17</sup> which is sometimes considered to be the most fundamental source of error in KS-DFT with approximate exchange-correlation functionals. MC-PDFT is also less prone than KS-DFT<sup>18</sup> to self-interaction error.

The decomposition of the MC-PDFT energy expression of eq 1 into its individual components is sometimes important for understanding chemical and physical phenomena in molecular systems.<sup>19,20</sup> This decomposition is available in *OpenMolcas*, along with the tabulation of  $\rho$  and  $\Pi$  in Cartesian coordinates for plotting and visualization.

## 1. On-top functionals for MC-PDFT

Due to the symmetry dilemma, the spin-polarized exchange-correlation functions of KS-DFT are not compatible with the spin-densities of a multiconfiguration wave function. To bypass the symmetry dilemma, we use translated<sup>1</sup> and fully translated<sup>21</sup> on-top functionals, which are obtained by translation of KS-DFT exchange-correlation functionals of the spin densities and their gradients. Translated functionals are denoted with the prefix “t,” and fully translated functionals are denoted with the prefix “ft.” If

$E_{xc}(\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r}), \nabla\rho_\alpha(\mathbf{r}), \nabla\rho_\beta(\mathbf{r}))$  denotes the KS-DFT exchange-correlation functional, in which  $\rho_\sigma$  is the spin density ( $\sigma = \alpha, \beta$ ), and  $\nabla\rho_\sigma$  is the gradient of the density, the translated functional is given by:

$$E_{ot}^{GGA}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|, \Pi(\mathbf{r})) = E_{xc}(\rho_\alpha^t(\mathbf{r}), \rho_\beta^t(\mathbf{r}), \nabla\rho_\alpha^t(\mathbf{r}), \nabla\rho_\beta^t(\mathbf{r})), \quad (3)$$

where

$$\rho_\alpha^t(\mathbf{r}) = \begin{cases} \frac{\rho}{2} \left( 1 + \sqrt{1 - \frac{4\Pi}{\rho^2}} \right), & \text{when } \frac{4\Pi}{\rho^2} \leq 1 \\ \frac{\rho}{2}, & \text{when } \frac{4\Pi}{\rho^2} > 1 \end{cases}$$

$$\rho_\beta^t(\mathbf{r}) = \begin{cases} \frac{\rho}{2} \left( 1 - \sqrt{1 - \frac{4\Pi}{\rho^2}} \right), & \text{when } \frac{4\Pi}{\rho^2} \leq 1 \\ \frac{\rho}{2}, & \text{when } \frac{4\Pi}{\rho^2} > 1 \end{cases}$$

$$\nabla\rho_\alpha^t(\mathbf{r}) = \begin{cases} \frac{\nabla\rho}{2} \left( 1 + \sqrt{1 - \frac{4\Pi}{\rho^2}} \right), & \text{when } \frac{4\Pi}{\rho^2} \leq 1 \\ \frac{\nabla\rho}{2}, & \text{when } \frac{4\Pi}{\rho^2} > 1 \end{cases}$$

$$\nabla \rho_{\beta}^t(\mathbf{r}) = \begin{cases} \frac{\nabla \rho}{2} \left( 1 - \sqrt{1 - \frac{4\Pi}{\rho^2}} \right), & \text{when } \frac{4\Pi}{\rho^2} \leq 1 \\ \frac{\nabla \rho}{2}, & \text{when } \frac{4\Pi}{\rho^2} > 1 \end{cases}$$

in which  $\nabla \rho$  is the gradient of the density. For a single-determinant wave function,  $\frac{4\Pi}{\rho^2} \leq 1$  in all space. However, for a multiconfiguration wave function, this ratio can be greater than one. Notice that the translated functionals depend on  $\Pi$  but not on its gradient and that they have a discontinuous derivative where  $\frac{4\Pi}{\rho^2} = 1$ .

Fully translated functionals also depend on  $\nabla \Pi$ , and the first and the second derivatives of the functional are continuous. Both kinds of functionals have been found to give reasonably good results for multireference systems.

*OpenMolcas* supports the use of several different on-top functionals, including a translated local spin-density approximation (LDA), various translated generalized gradient approximations, and various fully-translated generalized gradient approximations. The following is a list of currently supported functionals: tLSDA,<sup>1,22,23</sup> ftLSDA,<sup>22,23</sup> tPBE,<sup>1,24</sup> ftPBE,<sup>21,24</sup> trevPBE,<sup>25,26</sup> ftrevPBE,<sup>25,26</sup> tBLYP<sup>1,27,28</sup> ftBLYP,<sup>21,27,28</sup> tOPBE,<sup>29,24,30</sup> and ftOPBE.<sup>29,24,30</sup>

*OpenMolcas* also supports functionals obtained by scaling the exchange and/or correlation components of the exchange-correlation functionals prior to translation. The scaling factors may be input by a user. This allows the functionals to be modified into an HLE-type functional,<sup>31,32</sup> where the standard scaling factors are 1.25 for exchange and 0.5 for correlation, but the user may also choose other scaling factors.

## 2. Performance of MC-PDFT

MC-PDFT generally produces results that are comparable in accuracy to complete active space second-order perturbation theory (CASPT2) but at significantly lower computational cost<sup>33</sup> on bond energies,<sup>21,34,35,36,37</sup> spin-multiplet splittings,<sup>38,39,40,41</sup> and other excitation energies.<sup>42,43,44,45</sup> These results are summarized in Table 1. A review

containing references for tests and validations on electronically excited states up to mid-2018 is available.<sup>46</sup>

Table 1: Mean unsigned error (MUE) of MC-PDFT using tPBE functional and CASPT2

Reference	System	Property	MUE (eV)	
			PT2	tPBE
1	6 covalent or ionic diatomic	dissociation energy	0.3	0.3
34	10 transition metals with ligand	average bond energy	0.24	0.19
38	11 n-acene (from naphthalene to dodecacene)	singlet-triplet gap	0.06 <sup>a</sup>	0.13 <sup>a</sup>
39	13 main group atoms or compounds	singlet-triplet gap	0.12 <sup>b</sup>	0.24 <sup>b</sup>
40	8 organic rings	singlet-triplet gap	0.01 <sup>b</sup>	0.10 <sup>b</sup>
43	19 main group atoms	first excitation energy	0.22	0.42
45	10 doublet radicals	first 5 vertical excitation energy	0.14	0.19

<sup>a</sup>The reference wave function is optimized from a generalized active space (GAS) self-consistent calculation.<sup>5,47</sup>

<sup>b</sup>The active space for the reference wave function uses correlated-participation-orbital (CPO) scheme.<sup>48</sup>

### 3. Analytic gradients for SS-CAS-PDFT

*OpenMolcas* includes analytic gradients for MC-PDFT when a state-specific CASSCF (SS-CASSCF) wave function is used as a reference (SS-CAS-PDFT), and these gradients enable the fast and efficient determination of equilibrium and transition state structures.<sup>49</sup> Because MC-PDFT is a non-variational method, the computation of the gradient requires the construction of a Lagrangian. In general, the computation of analytic gradients can be performed at least an order of magnitude faster than the corresponding gradient calculation using a numerical finite-difference method. SS-CAS-PDFT shows good accuracy compared to experimental data for both equilibrium and transition-state structures. Some illustrative single-processor timings for MC-PDFT calculations

employing the tPBE on-top functional are shown in Table 2.

Table 2: Illustrative timings (in seconds) for a single gradient computation using a single processor.

	Active Space	Symmetry	cc-pVDZ		cc-pVTZ	
			CASPT2	tPBE	CASPT2	tPBE
NH <sub>3</sub>	(6,6)	C <sub>s</sub>	16	7	32	14
HCN	(8,8)	C <sub>2v</sub>	9	4	17	10
CH <sub>2</sub> O	(12,9)	C <sub>2v</sub>	29	9	29	15
HCCH	(10,10)	D <sub>2h</sub>	20	6	20	11
oxirane	(10,10)	C <sub>2v</sub>	55	27	136	45
pyrrole	(6,5)	C <sub>2v</sub>	87	39	1082	212
acrolein	(4,4)	C <sub>s</sub>	558	117	3390	160
butadiene	(4,4)	C <sub>2h</sub>	85	29	933	137
pyridine	(6,6)	C <sub>2v</sub>	183	32	2256	156
maleic anhydride	(8,7)	C <sub>2v</sub>	123	36	1148	218

#### 4. State-interaction pair-density functional theory

The accurate description of ground- and excited-state potential energy surfaces, in cases where two electronic states are strongly interacting (such as near conical intersections or locally avoided crossings) is a challenge for many electronic structure methods. We have introduced a new framework, called state-interaction PDFT (SI-PDFT),<sup>50</sup> to handle these situations, and this has been recently implemented in *OpenMolcas*. SI-PDFT is an extension of MC-PDFT that involves the diagonalization of an  $N \times N$  effective Hamiltonian to generate a new set of  $N$  electronic states with proper potential energy surface topology in regions of strong state interaction. This method is similar in spirit and application to the “perturb-then-diagonalize” approaches in multireference perturbation theories such as MS-CASPT2<sup>51,52</sup> or MC-QDPT.<sup>53,54</sup> An illustrative example is shown in Figure 1. The tPBE functional was used for both a standard MC-PDFT calculation and a SI-PDFT calculation. While unphysical curve crossings are present in the standard MC-PDFT treatment, these vanish when the SI-PDFT methodology is used because the final

step in the SI-PDFT method is a diagonalization.

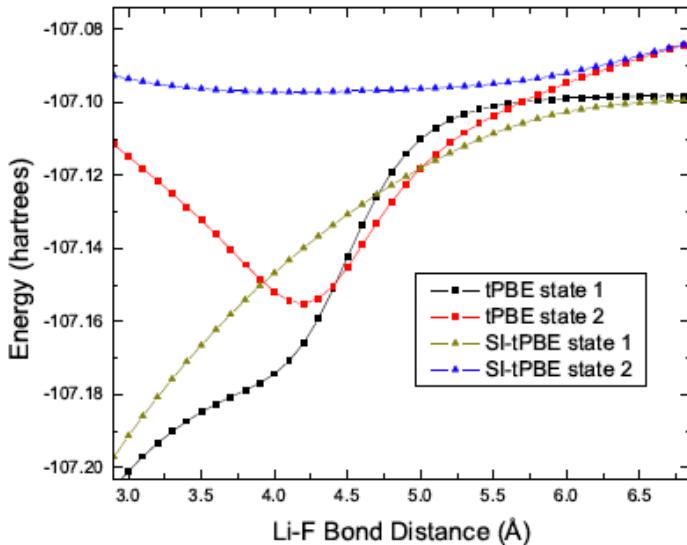


Figure 1. Dissociation of LiF calculated with a (6e,6o) active space.

## 5. Density matrix renormalization group pair density functional theory (DMRG-PDFT)

The density matrix renormalization group (DMRG) is a powerful method to treat static correlation, especially in molecular systems requiring large active-spaces. MC-PDFT can be used in conjunction with DMRG to add additional dynamic correlation in an inexpensive way.<sup>55</sup> The DMRG-PDFT implementation is based on an interface between the existing MC-PDFT code in *OpenMolcas* and the DMRG code in the *QC-MAQUIS*<sup>56,57,58</sup> program. An illustrative example of singlet-triplet gaps in polyacenes is shown in Fig 2. The tPBE/6-31G+(d,p) level of theory was used.

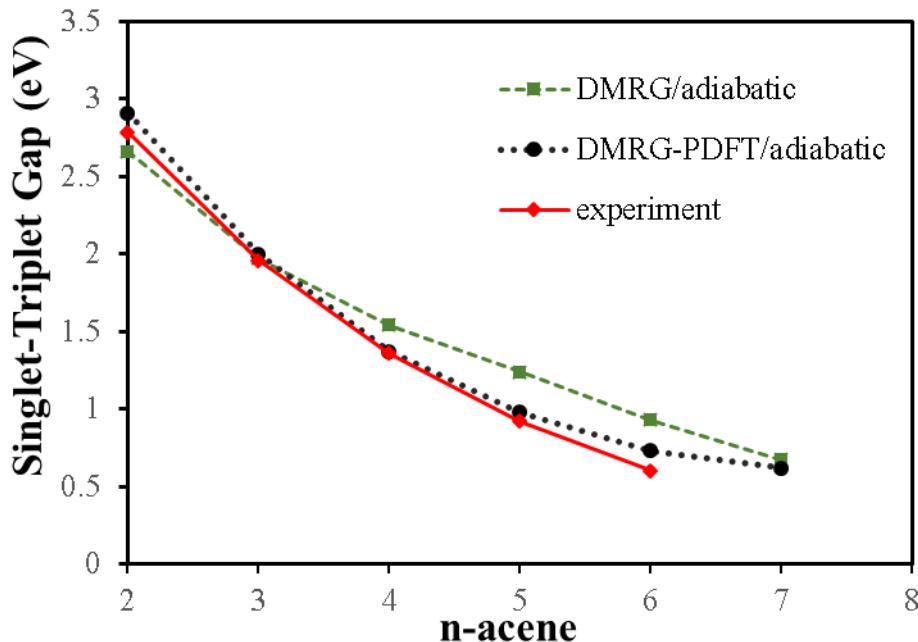


Figure 2. Singlet-triplet gaps in polyacenes.

## 6. Property integrals of individual orbitals

*OpenMolcas* supports the computation of property integrals including the multipole moments, Cartesian moments, electric potential, electric field, electric field gradients, diamagnetic shielding, and one-electron Darwin contact term of molecular orbitals in the *SEWARD* module. It supports any orbital calculated in the *SCF*, *RASSCF*, or *CASPT2* module. The sum of the occupation-number-weighted orbital property integral is the total electronic part of a property integral, so the occupation-number-weighted orbital property represents how much each orbital contributes to a property integral of an electronic state. One option is to print, for each molecular orbital, these property integrals weighted by the occupation number of each orbital, and the other option is to print these property integrals for each orbital without being weighted by the occupation numbers. If the property integral of an unoccupied orbital needs to be analyzed, the latter option is needed. The latter option can be useful when analyzing Rydberg states to determine which orbitals are Rydberg orbitals. This capability can also be useful when deciding which orbitals should be included in the active space. For these examples, to determine how diffuse each orbital is,

the second Cartesian moment  $\langle r^2 \rangle$  and its components ( $\langle x^2 \rangle$ ,  $\langle y^2 \rangle$ ,  $\langle z^2 \rangle$ ,  $\langle xy \rangle$ ,  $\langle xz \rangle$ ,  $\langle yz \rangle$ ) of each orbital should be calculated using the latter option. An example input file can be found in the Supporting Information.

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