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# Maximum radius of convergence perturbation theory

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An *ab initio* method is introduced, called the maximum radius of convergence ( $\text{MAXR}_c$ ) perturbation theory, that exploits the added degrees of freedom permitted with flexible energy denominator perturbation theory [J. Chem. Phys. **109**, 7725 (1998)] by defining the energy-denominator factors of a Rayleigh–Schrödinger perturbative expansion to be (approximately) optimal. This method can yield rapid convergence as long as there is no quasidegeneracies in first order between the reference-space state and one of the orthogonal-space states. © 2000 American Institute of Physics. [S0021-9606(00)30314-2]

## I. INTRODUCTION

Rayleigh–Schrödinger perturbation theory is a very successful *ab initio* method, especially when employed with Møller–Plesset partitioning for closed-shell ground-state systems.<sup>1–4</sup> However, the unrestricted formalisms<sup>5,6</sup> are widely considered to exhibit slow convergence that is related to the degree of spin contamination<sup>7,8</sup> and the magnitude of the radius of convergence.<sup>7</sup> Even for closed-shell ground states, Møller–Plesset partitioning is not always effective in higher order, where damping behavior may appear and—eventually—divergence.<sup>9,10</sup> Therefore, it is desirable to construct a method that offers some improvements, even though previous attempts have failed.<sup>11–13</sup>

The energy denominators of Rayleigh–Schrödinger perturbation theory are constructed from energy-denominator factors that are given by the zeroth-order energy differences between the reference-space state and the orthogonal-space states. Using a general form of the zeroth-order Hamiltonian  $H_0$ , it is easy to show that the zeroth-order energies of a perturbation expansion are arbitrary;<sup>14,15</sup> but, this choice is critical, since the convergence behavior depends to a great extent on the zeroth-order energies.<sup>14,16</sup> This dependence is most easily demonstrated by examining two-state systems where the radius of convergence  $R_c$  is easily computed and can be used to model the convergence difficulties for systems involving many states.<sup>16–18</sup>

The optimization (OPT) partitioning method<sup>16–18</sup> chooses the zeroth-order energies of the dominant states in an optimal manner. This method has been demonstrated to yield rapid convergence for perturbation calculations that are known to converge poorly with Møller–Plesset and Epstein–Nesbet<sup>19–21</sup> partitionings. (A similar method, also called optimization partitioning, is based on optimizing the energy denominator shifts using a variational form of the first-order wave function.)<sup>22</sup> Unfortunately, the OPT partitioning method does not possess a linked diagram formalism, since its energy denominators are based on the Hilbert space, instead of the Fock space. We wish to obtain a method that is similar to OPT partitioning, but is size extensive and possesses a linked diagram theorem (LDT). One method is to

optimize the orbital energies using a Fock space. This approach, however, is less than ideal, since there are only a small number of parameters—the orbital energies—to optimize, especially compared to the huge number of determinantal states within the Hilbert space.

Flexible energy denominator perturbation theory<sup>23</sup> is a general formalism for inserting additional parameters—one-, two-, and higher-body shifts—into the energy denominators of a Rayleigh–Schrödinger perturbation expansion, in a manner that preserves the LDT. Below we introduce a method, maximum radius of convergence ( $\text{MAXR}_c$ ) perturbation theory, that exploits the added degrees of freedom permitted with flexible-energy denominators, by defining its energy denominator factors to be (approximately) optimal. Explicitly, in  $\text{MAXR}_c$  perturbation theory, the energy denominator factors arising between the reference-space state  $|p\rangle$  and any orthogonal-space state, say  $|q\rangle$ , are defined so that it yields a maximum radius of convergence, if used in a two-state perturbation expansion involving *only* these two states,  $|p\rangle$  and  $|q\rangle$ .

The  $\text{MAXR}_c$  approach enlarges the energy denominator factors associated with two states,  $|p\rangle$  and  $|q\rangle$ , when the coupling between these states are enlarged or their Hamiltonian expectation values become closer. In cases where there is no coupling between  $|p\rangle$  and  $|q\rangle$ , the energy denominators reduce to their values in Epstein–Nesbet partitioning. The  $\text{MAXR}_c$  method can yield rapid convergence, provided the Hamiltonian expectation value of the reference state and any state from the orthogonal space is not close: no first-order quasidegeneracies. Note that small energy denominators caused by zeroth-order degeneracies do not occur, but can appear in other partitioning methods. If the energy denominator shifts are neglected and Hartree–Fock canonical orbitals are used, the  $\text{MAXR}_c$  method reduces to Møller–Plesset perturbation theory.

While the final energies and wave functions of coupled cluster theory<sup>24</sup> do not depend on a zeroth-order Hamiltonian  $H_0$ , the coupled cluster equations can be solved by introducing an  $H_0$  and, therefore, also energy-denominator factors. In Lindgren’s formulations,<sup>25</sup> the coupled-cluster equations are

derived from perturbation theory, and a pseudodependence on  $H_0$  appear in the final equations. Using this type of formulation, the  $\text{MAXR}_c$  approach combined with flexible-energy denominators can be employed to enhance the iterative convergence of coupled-cluster equations. Alternately, using a perturbative expansion, an infinite-order summation of all connected wave-operator diagrams can be used to obtain the cluster operator  $T$ , which defines the exponential form the wave operator  $e^T$ .

In Sec. II the energy denominator factor that yields that maximum radius of convergence for a two-state system is derived. This relationship is used to define the energy denominator shifts for  $\text{MAXR}_c$  perturbation theory, presented in Sec. III. A spin-adapted, closed-shell, restricted-orbital formalism is presented in Secs. IV and V.

## II. MAXIMUM RADIUS OF CONVERGENCE FOR A TWO-STATE SYSTEM

Denote  $|p\rangle$  and  $|q\rangle$  as the reference ( $P$ ) and orthogonal ( $Q$ ) space states of a two-dimensional system, and  $\epsilon_p$  and  $\epsilon_q$  as their zeroth-order energies. These zeroth-order energies are arbitrary and define the diagonal, zeroth-order Hamiltonian,

$$H_0 = |p\rangle\epsilon_p\langle p| + |q\rangle\epsilon_q\langle q|. \quad (2.1)$$

The radius of convergence  $R_c$  for the two-state, Rayleigh–Schrödinger perturbation expansion is easily derived (see, for example, Chaudhuri and coworkers),<sup>18</sup>

$$R_c^2 = \frac{\epsilon^2}{(\epsilon - H_p^q)^2 + 4|\langle p|H|q\rangle|^2}, \quad (2.2)$$

where

$$R_c \geq 0, \quad (2.3)$$

$$H_p^q = \langle p|H|p\rangle - \langle q|H|q\rangle, \quad (2.4)$$

and  $\epsilon$  is the sole energy-denominator factor appearing in the perturbation expansion,

$$\epsilon = \epsilon_p - \epsilon_q. \quad (2.5)$$

The perturbation expansion is convergent if  $R_c \geq 1$ , and divergent if  $0 \leq R_c < 1$ .

We wish to choose  $\epsilon$  so that it yields the maximum radius of convergence  $R_c$ . This value of  $\epsilon$ , denoted as  $\epsilon_m(pq)$ , satisfies

$$\left[ \frac{\partial}{\partial \epsilon} R_c^2 \right]_{\epsilon = \epsilon_m(pq)} = 0. \quad (2.6)$$

Substituting Eq. (2.2) into Eq. (2.6) gives

$$\epsilon_m(pq) = H_p^q + \frac{4|\langle p|H|q\rangle|^2}{H_p^q}. \quad (2.7)$$

Note that  $\epsilon_m(pq)$  has the same sign as  $H_p^q$ . This relationship is expected, since for a two-state system  $\epsilon$  and  $H_p^q$  must have the same sign or  $R_c < 1$ .<sup>16,17</sup>

In the limit of the coupling  $\langle p|H|q\rangle$  vanishing, the maximum  $R_c$  is given by Epstein–Nesbet partitioning,

$$\epsilon_m(pq) = H_p^q \quad \text{for } |\langle p|H|q\rangle| \rightarrow 0. \quad (2.8)$$

When the second term on the right-hand-side of Eq. (2.7) dominates, we get

$$\epsilon_m(pq) \approx \frac{4|\langle p|H|q\rangle|^2}{H_p^q} \quad \text{for } \frac{4|\langle p|H|q\rangle|^2}{H_p^q} \gg H_p^q. \quad (2.9)$$

Thus, in situations where the ratio  $4|\langle p|H|q\rangle|^2/H_p^q$  is large,  $\epsilon_m(pq)$  is also large. Traditional partitioning methods have zeroth-order energy differences that do not depend on the coupling  $\langle p|H|q\rangle$  between states. Thus, not surprisingly, when  $|\langle p|H|q\rangle|^2/H_p^q$  is even modestly large, these methods often yield divergent expansions. We wish to obtain a perturbative method that enlarges  $\epsilon$  as  $|\langle p|H|q\rangle|^2/H_p^q$  becomes large, and selects  $\epsilon$  so that it has the same sign as  $H_p^q$ .

It is also easy to obtain the value of  $\epsilon$ , denoted by  $\epsilon_1(pq)$ , that yield a radius of convergence equal to unity ( $R_c = 1$ ),<sup>16,17</sup>

$$\epsilon_1(pq) = \frac{1}{2} \left( H_p^q + \frac{4|\langle p|H|q\rangle|^2}{H_p^q} \right). \quad (2.10)$$

Comparing Eqs. (2.7) and (2.10) we find that

$$\epsilon_1(pq) = \frac{1}{2} \epsilon_m(pq). \quad (2.11)$$

Since, for a two state system, it is always possible to choose  $\epsilon$  so that ( $R_c > 1$ ),<sup>14,16</sup> then, clearly, the maximum radius of convergence also has a value greater than unity. However, if there is a first-order quasidegeneracy,  $H_p^q = 0$ , then Eqs. (2.7) and (2.11) yield infinities, [ $\epsilon_1(pq) = \infty$ ] and [ $\epsilon_m(pq) = \infty$ ].

## III. MAXIMUM RADIUS OF CONVERGENCE PERTURBATION THEORY

### A. Qualitative development

The energy-denominator factors for Rayleigh–Schrödinger perturbation theory<sup>4,25–28</sup> are given by the zeroth-order energy differences between pairs of interspace states, where a pair of interspace states consists of the reference-space state  $|p\rangle$  and a state, say  $|q\rangle$ , from the orthogonal space  $Q$ . As a simple example, consider Møller–Plesset perturbation theory.<sup>2,3</sup> Its first-order wave function (and second-order energy) consists of terms arising from double excitations from  $|p\rangle$ :  $w, x \rightarrow r, s$ ; these excitations have an associated energy-denominator factor, denoted by  $\epsilon_{wx}^{rs}$ , given by

$$\begin{aligned} \epsilon_{wx}^{rs} &= \epsilon_w + \epsilon_x - \epsilon_r - \epsilon_s = \langle p|H_0|p\rangle - \langle q|H_0|q\rangle, \\ |q\rangle &= a_r^\dagger a_s^\dagger a_x a_w |p\rangle, \end{aligned} \quad (3.1)$$

where the zeroth-order Hamiltonian  $H_0$  is the Hartree–Fock Hamiltonian and the orbital energies  $\epsilon_i$  are eigenvalues of the Fock operator.<sup>4</sup> (Note that the second-order wave function consists of terms that have two energy-denominator factors.)

In a perturbation expansion involving *only* two states,  $|p\rangle$  and  $|q\rangle$ , the zeroth-order energy difference can be determined that yields the maximum  $R_c$ , as demonstrated in the previous section. In Sec. III (B), a formalism is presented

that employs these two-state, zeroth-order energy differences (or energy-denominator factors) in a perturbation expansion involving the reference-space state  $|p\rangle$  and simultaneously *all* the orthogonal-space states; where, the orthogonal states of interests are generated by applying excitation operators to  $|p\rangle$ :  $a_r^\dagger a_w |p\rangle$ ,  $a_r^\dagger a_s^\dagger a_x a_w |p\rangle$ ,  $a_r^\dagger a_s^\dagger a_t^\dagger a_y a_x a_w |p\rangle$ , . . . .

In order to increase the degrees of freedom in choosing the energy-denominator factors, one-body energy-denominator shifts  $\Delta_w^r$  are added to the energy-denominator factors corresponding to single excitations, two-body shifts  $\Delta_{wx}^{rs}$  for double excitations, and so on. If we denote the energy-denominator factors from single, double, and triple excitations by  $\epsilon_w^r$ ,  $\epsilon_{wx}^{rs}$ , and  $\epsilon_{wxy}^{rst}$ , respectively, then these factors are given by

$$\epsilon_w^r = \epsilon_w - \epsilon_r + \Delta_w^r, \quad (3.2)$$

$$\epsilon_{wx}^{rs} = \epsilon_w + \epsilon_x - \epsilon_r - \epsilon_s + \Delta_{wx}^{rs}, \quad (3.3)$$

$$\epsilon_{wxy}^{rst} = \epsilon_w + \epsilon_x + \epsilon_y - \epsilon_r - \epsilon_s - \epsilon_t + \Delta_{wxy}^{rst}, \quad (3.4)$$

where  $w$ ,  $x$ , and  $y$  are occupied orbitals and  $r$ ,  $s$ , and  $t$  are virtuals. The energy-denominator shifts,  $\Delta_w^r$ ,  $\Delta_{wx}^{rs}$ ,  $\Delta_{wxy}^{rst}$ , and  $\Delta_{wxyz}^{rstu}$ , can be introduced in a manner that preserves the LDT, as long as additional perturbations are added and disconnected products are treated in a special manner.<sup>23</sup>

In summary, the energy-denominator factors for MAXR<sub>c</sub> perturbation theory are given by Eqs. (3.2), (3.3), and (3.4) with  $\Delta_w^r$  defined so that a perturbation expansion involving *only* the reference state  $|p\rangle$  and  $a_r^\dagger a_w |p\rangle$  has the maximum  $R_c$ . Similarly,  $\Delta_{wx}^{rs}$  is chosen so that the expansion for  $|p\rangle$  and  $a_r^\dagger a_s^\dagger a_x a_w |p\rangle$  has a maximum  $R_c$ . (Higher-body shifts are defined in a similar manner.) This formalism reduces to Møller–Plesset perturbation theory when Hartree–Fock canonical orbitals are used and the shifts are neglected.

### B. Mathematical development

We now derive the one-, two-, and three-body, energy-denominator shifts:  $\Delta_w^r$ ,  $\Delta_{wx}^{rs}$ , and  $\Delta_{wxy}^{rst}$ , using Eqs. (3.2), (3.3), (3.4), and (2.7). The energy-denominator factors for the single excitations are defined by

$$\epsilon_w^r = \epsilon_m(pq) \quad \text{for } |q\rangle = a_r^\dagger a_w |p\rangle. \quad (3.5)$$

Substituting Eq. (3.5) into Eq. (2.7) and using Eq. (3.2), we get

$$\Delta_w^r = G_{rw} + \frac{4|\epsilon_{rw}|^2}{G_{rw} + \epsilon_w - \epsilon_r}, \quad (3.6)$$

where

$$\epsilon_{ij} = [i|h|j] + \sum_w [ij|ww] - [iw|wj], \quad (3.7)$$

$$\epsilon_i = \epsilon_{ii}, \quad (3.8)$$

$$G_{rw} = [rr|ww] - [rw|wr], \quad (3.9)$$

and the spin-dependent one- and two-electron integrals are written using chemist's notation.<sup>4</sup>

Similarly, the energy-denominator factors for the doubly excitations are defined by

$$\epsilon_{wx}^{rs} = \epsilon_m(pq) \quad \text{for } |q\rangle = a_r^\dagger a_s^\dagger a_x a_w |p\rangle. \quad (3.10)$$

Substituting Eq. (3.10) into Eq. (2.7) and using Eq. (3.3), we get

$$\Delta_{wx}^{rs} = G_{wx}^{rs} + \frac{4|[wr|xs] - [ws|xr]|^2}{G_{wx}^{rs} + \epsilon_w + \epsilon_x - \epsilon_r - \epsilon_s}, \quad (3.11)$$

where

$$G_{wx}^{rs} = G_{rw} + G_{rx} + G_{sw} + G_{sx} - G_{rs} - G_{wx}. \quad (3.12)$$

The energy-denominator factors for the triple excitations are defined by

$$\epsilon_{wxy}^{rst} = \epsilon_m(pq) \quad \text{for } |q\rangle = a_r^\dagger a_s^\dagger a_t^\dagger a_y a_x a_w |p\rangle. \quad (3.13)$$

Since triply excited states  $a_r^\dagger a_s^\dagger a_t^\dagger a_y a_x a_w |p\rangle$  do not couple with  $|p\rangle$  via the Hamiltonian  $H$ ,

$$\langle q|H|p\rangle = 0, \quad (3.14)$$

the energy-denominator factors for these excitations are the same as they appear in Epstein–Nesbet partitioning. By substituting Eqs. (3.13) and (3.14) into Eq. (2.7) we get

$$\epsilon_{wxy}^{rst} = \langle p|H|p\rangle - \langle q|H|q\rangle, \quad |q\rangle = a_r^\dagger a_s^\dagger a_t^\dagger a_y a_x a_w |p\rangle. \quad (3.15)$$

Using Eq. (3.4) gives

$$\Delta_{wxy}^{rst} = {}^{ov}G_{wxy}^{rst} - {}^{oo}G_{wxy} - {}^{vv}G_{rst}, \quad (3.16)$$

where the occupied-virtual  ${}^{ov}G_{wxy}^{rst}$ , occupied-occupied  ${}^{oo}G_{wxy}$ , and virtual-virtual  ${}^{vv}G_{rst}$  terms are given by

$$\begin{aligned} {}^{ov}G_{wxy}^{rst} &= G_{rw} + G_{rx} + G_{ry} + G_{sw} + G_{sx} + G_{sy} \\ &\quad + G_{tw} + G_{tx} + G_{ty}, \end{aligned} \quad (3.17)$$

$${}^{oo}G_{wxy} = G_{wx} + G_{wy} + G_{xy}, \quad (3.18)$$

$${}^{vv}G_{rst} = G_{rs} + G_{rt} + G_{st}. \quad (3.19)$$

By generalizing these three latter expressions, higher-body shifts  $\Delta_{wxyz}^{rstu}$  are easily obtained.

### IV. CLOSED-SHELL RESTRICTED SPIN-ORBITAL FORMALISM

We now obtain the spin-independent forms for the energy-denominator factors ( $\epsilon_w^r$ ,  $\epsilon_{wx}^{rs}$ ,  $\epsilon_{wxy}^{rst}$ ) and shifts ( $\Delta_w^r$ ,  $\Delta_{wx}^{rs}$ ,  $\Delta_{wxy}^{rst}$ ) for a spin-free Hamiltonian when the  $\alpha$  and  $\beta$  spin-orbitals are spatially restricted and all occupied orbitals are double occupied. Henceforth, all orbital indices refer to spatial orbitals. Spin-orbitals are indicated by appending the spin functions ( $\sigma = \alpha$  or  $\beta$ ) to the spatial orbitals. Also, we use a Goldstone diagrammatic representation,<sup>26</sup> since Hugenholtz<sup>27</sup> and Brandow<sup>29</sup> diagrams are antisymmetric and not readily converted into a spin-free form.

The spin-orbitals  $w\sigma$  and  $r\sigma'$  from the one-body energy-denominator factors  $\epsilon_{w\sigma}^{r\sigma'}$  can have either parallel or opposite spins. In the Goldstone diagrams in which these orbitals appear, they are on the same path. Spin-orbitals on the same path must have parallel spin or the diagrams

vanish.<sup>28,30</sup> Hence, only one-body energy-denominator factors  $\varepsilon_{w\sigma}^{r\sigma'}$  with parallel spins ( $\sigma = \sigma'$ ) need to be considered, and are given by

$$\varepsilon_{w\sigma}^{r\sigma} = \varepsilon_w^r = \varepsilon_w - \varepsilon_r + \Delta_w^r, \quad (4.1)$$

where

$$\Delta_w^r = \frac{4|\varepsilon_{wr}|^2}{\varepsilon_w - \varepsilon_r + g_{wr}(1)} + g_{wr}(1) \quad (4.2)$$

$$\varepsilon_{ij} = (i|h|j) + \sum_w 2(ij|ww) - (iw|wj), \quad (4.3)$$

$$\varepsilon_i = \varepsilon_{ii}, \quad (4.4)$$

$$g_{ij}(\eta) = (ii|jj) - \eta(ij|ji). \quad (4.5)$$

When evaluating diagrams with two-body energy-denominator factors  $\varepsilon_{w\sigma_1 x\sigma_3}^{r\sigma_2 s\sigma_4}$ , we use the convention that the spin-orbitals  $w\sigma_1$  and  $r\sigma_2$  are on the same path; also,  $x\sigma_3$  and  $s\sigma_4$  are on the same path. Diagrams vanish when spin-orbitals have opposite spin that are on the same path, when either  $\sigma_1 \neq \sigma_2$  or  $\sigma_3 \neq \sigma_4$ . Therefore, we have only two cases to consider for the restricted-orbital, two-body, energy-denominator factors:

$$\varepsilon_{w\sigma x\sigma'}^{r\sigma s\sigma'} = \varepsilon_w - \varepsilon_r + \varepsilon_x - \varepsilon_s + \begin{cases} {}^1\Delta_{wx}^{rs} & \text{if } \sigma = \sigma' \\ {}^0\Delta_{wx}^{rs} & \text{if } \sigma \neq \sigma', \end{cases} \quad (4.6)$$

where

$$\eta\Delta_{wx}^{rs} = g_{wx}^{rs}(\eta) + \frac{4|(wr|xs) - \eta(ws|xr)|^2}{(\varepsilon_w - \varepsilon_r) + (\varepsilon_x - \varepsilon_s) + g_{wx}^{rs}(\eta)}, \quad (4.7)$$

$$g_{wx}^{rs}(\eta) = g_{rw}(1) + g_{sx}(1) + f_{wx}^{rs}(\eta), \quad (4.8)$$

$$f_{wx}^{rs}(\eta) = g_{sw}(\eta) + g_{rx}(\eta) - g_{rs}(\eta) - g_{wx}(\eta). \quad (4.9)$$

For diagrams with three-body, energy-denominator factors  $\varepsilon_{w\sigma_1 x\sigma_3 y\sigma_5}^{r\sigma_2 s\sigma_4 t\sigma_6}$  we use the convention that orbitals  $w\sigma_1$ ,  $x\sigma_3$ , and  $y\sigma_5$  are on the same path as  $r\sigma_2$ ,  $s\sigma_4$ , and  $t\sigma_6$ , respectively. Therefore, we have only three cases to consider:

$$\varepsilon_{w\sigma x\sigma' y\sigma''}^{r\sigma s\sigma' t\sigma''} = \varepsilon_w + \varepsilon_x + \varepsilon_y - \varepsilon_r - \varepsilon_s - \varepsilon_t + \begin{cases} (111)\Delta_{wxy}^{rst}; & \sigma = \sigma', \quad \sigma = \sigma'', \quad \sigma' = \sigma'' \\ (100)\Delta_{wxy}^{rst}; & \sigma \neq \sigma', \quad \sigma \neq \sigma'', \quad \sigma' = \sigma'' \\ (010)\Delta_{wxy}^{rst}; & \sigma \neq \sigma', \quad \sigma = \sigma'', \quad \sigma' \neq \sigma'' \\ (001)\Delta_{wxy}^{rst}; & \sigma = \sigma', \quad \sigma \neq \sigma'', \quad \sigma' \neq \sigma'' \end{cases} \quad (4.10)$$

where

$$\begin{aligned} (abc)\Delta_{wxy}^{rst} &= g_{rw}(1) + g_{sx}(1) + g_{ty}(1) + f_{xy}^{st}(a) \\ &\quad + f_{wy}^{rt}(b) + f_{wx}^{rs}(c). \end{aligned} \quad (4.11)$$

## V. SPIN-ADAPTED ENERGY-DENOMINATOR FACTORS

The choice of  $\varepsilon_{w\sigma x\sigma'}^{r\sigma s\sigma'}$  and  $\varepsilon_{w\sigma x\sigma' y\sigma''}^{r\sigma s\sigma' t\sigma''}$  given in Eqs. (4.6) and (4.10) generates perturbation expansions with wave functions that are not eigenfunctions of  $S^2$ . For two-body energy-denominator factors, this spin contamination appears because, in general,

$${}^0\Delta_{wx}^{rs} \neq {}^1\Delta_{wx}^{rs}. \quad (5.1)$$

A spin-adapted choice for the two-body factors  $\varepsilon_{w\sigma x\sigma'}^{r\sigma s\sigma'}$ , that is spin-adapted, is given by

$$\varepsilon_{w\sigma x\sigma'}^{r\sigma s\sigma'} = \varepsilon_{wx}^{rs}, \quad (5.2)$$

where  $\varepsilon_{wx}^{rs}$  is defined by Eq. (3.3) with orbital indices denoting spatial orbitals and the spin-independent shift  $\Delta_{wx}^{rs}$  defined by averaging the two  $\eta$  values,

$$\Delta_{wx}^{rs} = 1/2({}^0\Delta_{wx}^{rs} + {}^1\Delta_{wx}^{rs}). \quad (5.3)$$

As an alternative, an average of the two possible spin-dependent shifts is taken,

$$\Delta_{wx}^{rs} = \frac{1}{2}({}^0\Delta_{wx}^{rs} + {}^1\Delta_{wx}^{rs}). \quad (5.4)$$

A third and more conservative choice is given by

$$\Delta_{wx}^{rs} = \begin{cases} {}^0\Delta_{wx}^{rs} & \text{if } |{}^0\varepsilon_{wx}^{rs}| > |{}^1\varepsilon_{wx}^{rs}| \\ {}^1\Delta_{wx}^{rs} & \text{if } |{}^1\varepsilon_{wx}^{rs}| > |{}^0\varepsilon_{wx}^{rs}|. \end{cases} \quad (5.5)$$

When there is a repeated index, either ( $r=s$ ) and ( $w=x$ ), then we must have ( $\sigma \neq \sigma'$ ). Therefore, for this case, we should choose ( $\Delta_{wx}^{rs} = {}^0\Delta_{wx}^{rs}$ ).

As in the two-body case, the spin contamination arise from the three-body energy-denominator shifts, because, in general,

$${}^{(abc)}\Delta_{wxy}^{rst} \neq {}^{(a'b'c')} \Delta_{wxy}^{rst} \quad \text{if } abc \neq a'b'c'. \quad (5.6)$$

This problem is removed by choosing

$$\varepsilon_{w\sigma x\sigma' y\sigma''}^{r\sigma s\sigma' t\sigma''} = \varepsilon_{wxy}^{rst}, \quad (5.7)$$

where  $\varepsilon_{wxy}^{rst}$  is given by Eq. (3.4) and the spin-independent shift  $\Delta_{wxy}^{rst}$  taken as an average of the four possible spin-dependent shifts, or equivalently, averaging  $\eta$ ,

$$\begin{aligned} \Delta_{wxy}^{rst} &= \frac{1}{4}({}^{(111)}\Delta_{wxy}^{rst} + {}^{(100)}\Delta_{wxy}^{rst} + {}^{(010)}\Delta_{wxy}^{rst} + {}^{(001)}\Delta_{wxy}^{rst}) \\ &= \frac{1}{2} \frac{1}{2} \frac{1}{2} \Delta_{wxy}^{rst}. \end{aligned} \quad (5.8)$$

As in the two-body shifts  $\Delta_{wx}^{rs}$ , a modified expression should be used for the three-body shifts  $\Delta_{wxy}^{rst}$  when one or more indices are repeated. For example, if ( $r=s$ ) then  $\Delta_{wxy}^{rrt}$  should be taken as an average of  ${}^{(100)}\Delta_{wxy}^{rrt}$  and  ${}^{(010)}\Delta_{wxy}^{rrt}$ . Other choices like, for example, generalizing the two-body conservative choice given by Eq. (5.5), can also be used. However, since there is no coupling between the reference state  $|p\rangle$  and triply-excited states, the average choice, given by Eq. (5.8), should be sufficient in most cases.

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