

# Supplemental material for “Bridging single- and multireference domains for electron correlation: spin-extended coupled electron pair approximation”

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# 1 Introduction

In this material, we collect the expressions of matrices needed for ECEPA. We will use  $p, q, r, s$  for general spin-orbitals, and  $i, j, k, l$  and  $a, b, c, d$  for occupied and virtual spin-orbitals. The Einstein summation convention is assumed except for the summation over grid point  $g$ .

We also list some of the raw data obtained in this work to facilitate the comparison with other methods.

## 2 SUHF

The spin-projection operator in our work is conveniently written as

$$\hat{\mathcal{P}} \approx \sum_g^{N_{\text{grid}}} w_g \hat{R}_g, \quad (1)$$

where  $w_g$  are some weight, and  $\hat{R}_g$  is a unitary rotation operator. Applying it to a Slater determinant  $|\Phi\rangle$ , one obtains a SUHF wave function that is expanded as a linear combination of nonorthogonal Slater determinants  $|\Phi_g\rangle \equiv \hat{R}_g|\Phi\rangle$  according to Eq.(1). The SUHF energy

$$E_{\text{SUHF}} = \frac{\sum_g w_g \langle \Phi | \hat{H} | \Phi_g \rangle}{\sum_g w_g \langle \Phi | \Phi_g \rangle} = \frac{\sum_g w_g n_g E_g}{\sum_g w_g n_g} \quad (2)$$

is variationally minimized by rotating molecular orbitals of  $|\Phi\rangle$ . Here we defined

$$E_g = \frac{\langle \Phi | \hat{H} | \Phi_g \rangle}{\langle \Phi | \Phi_g \rangle} = \langle \Phi | \hat{H} | \Phi_g \rangle_N, \quad (3)$$

$$n_g = \langle \Phi | \Phi_g \rangle, \quad (4)$$

where subscript  $N$  indicates the matrix element is divided by  $n_g$ .

According to the nonorthogonal Wick theorem, we define the contraction matrix at each

grid  $g$

$$(\mathcal{W}_g)_{ij} = \langle \Phi | a_j^\dagger \hat{R}_g a_i | \Phi \rangle_N = (\mathbf{R}_g^{\text{oo}})_{ij}^{-1}, \quad (5)$$

$$(\mathcal{W}_g)_{ai} = \langle \Phi | a_i^\dagger a_a \hat{R}_g | \Phi \rangle_N = (\mathbf{R}_g^{\text{vo}} (\mathbf{R}_g^{\text{oo}})^{-1})_{ai}, \quad (6)$$

$$(\mathcal{W}_g)_{ia} = \langle \Phi | \hat{R}_g a_a^\dagger a_i | \Phi \rangle_N = ((\mathbf{R}_g^{\text{oo}})^{-1} \mathbf{R}_g^{\text{ov}})_{ia}, \quad (7)$$

$$(\mathcal{W}_g)_{ab} = \langle \Phi | a_a \hat{R}_g a_b^\dagger | \Phi \rangle_N = (\mathbf{R}_g^{\text{vv}} - \mathbf{R}_g^{\text{vo}} (\mathbf{R}_g^{\text{oo}})^{-1} \mathbf{R}_g^{\text{ov}})_{ab}, \quad (8)$$

where  $\mathbf{R}_g$  is the matrix representation of  $\hat{R}_g$  and, o and v indicate occupied and virtual spaces. The transition density matrix of SUHF

$$(\boldsymbol{\rho}_g)_{pq} = \langle \Phi | \hat{E}_{qp} | \Phi_g \rangle_N \quad (9)$$

is then

$$\boldsymbol{\rho}_g = \begin{pmatrix} \mathbf{1}^{\text{oo}} & \mathbf{0}^{\text{ov}} \\ \mathcal{W}_g^{\text{vo}} & \mathbf{0}^{\text{vv}} \end{pmatrix}. \quad (10)$$

The transition Fock matrix can be given by

$$(\mathbf{F}_g)_{pq} = h_{pq} + \langle pr || qs \rangle (\boldsymbol{\rho}_g)_{sr}, \quad (11)$$

which then allows us to write

$$E_g = h_{pq} (\boldsymbol{\rho}_g)_{qp} + \frac{1}{2} \langle pr || qs \rangle (\boldsymbol{\rho}_g)_{qp} (\boldsymbol{\rho}_g)_{sr}. \quad (12)$$

In what follows, it proves convenient to define the left- and right-transformation matrices

as

$$\mathcal{L}_g = \begin{pmatrix} \mathcal{W}_g^{\text{oo}} & \mathbf{0}^{\text{ov}} \\ -\mathcal{W}_g^{\text{vo}} & \mathbf{1}^{\text{vv}} \end{pmatrix}, \quad (13)$$

$$\mathcal{R}_g = \begin{pmatrix} \mathbf{1}^{\text{oo}} & \mathbf{0}^{\text{ov}} \\ \mathcal{W}_g^{\text{vo}} & \mathcal{W}_g^{\text{vv}} \end{pmatrix}, \quad (14)$$

and transform the transition Fock matrix and the bare two-electron integrals in the following manner:

$$\tilde{\mathcal{F}}_g := \mathcal{L}_g \mathbf{F}_g \mathcal{R}_g, \quad (15)$$

$$(\tilde{\mathcal{V}}_g)_{rs}^{pq} := (\mathcal{L}_g)_{pt} (\mathcal{L}_g)_{qu} \langle tu || vw \rangle (\mathcal{R}_g)_{vr} (\mathcal{R}_g)_{ws}. \quad (16)$$

### 3 ECISD

The ECISD energy is similarly given by

$$\mathcal{E} = \frac{\langle \Psi | \hat{H} \hat{\mathcal{P}} | \Psi \rangle}{\langle \Psi | \hat{\mathcal{P}} | \Psi \rangle} = \mathcal{E} = \frac{\sum_g w_g n_g \mathcal{E}_g}{\sum_g w_g n_g \mathcal{N}_g}, \quad (17)$$

where we have defined

$$\begin{aligned} \mathcal{E}_g &= \langle \Psi | \hat{H} | \Psi_g \rangle_N \\ &= h_{\mu\nu} \langle \Psi | a_\mu^\dagger a_\nu | \Psi_g \rangle_N + \frac{1}{4} \langle \mu\nu || \lambda\sigma \rangle \langle \Psi | a_\mu^\dagger a_\nu^\dagger a_\sigma a_\lambda | \Psi_g \rangle_N, \end{aligned} \quad (18)$$

$$\mathcal{N}_g = \langle \Psi | \Psi_g \rangle_N, \quad (19)$$

with  $|\Psi_g\rangle \equiv \hat{R}_g|\Psi\rangle$ . These terms are easily evaluated by using the sigma-vectors,

$$\langle\Phi|\hat{H}|\Psi_g\rangle_N = E_g\tilde{c}_0 + \tilde{\mathcal{F}}_{kc}\tilde{c}_k + \frac{1}{4}\bar{\mathcal{V}}_{cd}^{kl}c_{kl}^c, \quad (20a)$$

$$\begin{aligned} \langle\Phi_i^a|\hat{H}|\Psi_g\rangle_N &= \langle\Phi|\hat{H}|\Psi_g\rangle_N\mathcal{W}_{ai} + \tilde{\mathcal{F}}_{ai}\tilde{c}_0 + \left(E_g\mathcal{W}_{ac}\mathcal{W}_{ki} + \tilde{\mathcal{F}}_{ac}\mathcal{W}_{ki} - \mathcal{W}_{ac}\tilde{\mathcal{F}}_{ki} + \bar{\mathcal{V}}_{ic}^{ak}\right)\tilde{c}_k^c \\ &+ \left(\mathcal{W}_{ac}\mathcal{W}_{ki}\tilde{\mathcal{F}}_{ld} + \frac{1}{2}\mathcal{W}_{ki}\bar{\mathcal{V}}_{cd}^{al} - \frac{1}{2}\mathcal{W}_{ac}\bar{\mathcal{V}}_{id}^{kl}\right)c_{kl}^c, \end{aligned} \quad (20b)$$

$$\begin{aligned} \langle\Phi_{ij}^{ab}|\hat{H}|\Psi_g\rangle_N &= \mathcal{P}(ij)\mathcal{P}(ab)\left\{\langle\Phi_i^a|\hat{H}|\Psi_g\rangle_N\mathcal{W}_{bj} + \frac{1}{4}\bar{\mathcal{V}}_{ij}^{ab}\tilde{c}_0 - \frac{1}{2}E_g\mathcal{W}_{ai}\mathcal{W}_{bj}\tilde{c}_0 \right. \\ &+ \left(\mathcal{W}_{ac}\mathcal{W}_{ki}\tilde{\mathcal{F}}_{bj} - \frac{1}{2}\mathcal{W}_{ai}\mathcal{W}_{bj}\tilde{\mathcal{F}}_{kc} + \frac{1}{2}\mathcal{W}_{ac}\bar{\mathcal{V}}_{ij}^{bk} + \frac{1}{2}\mathcal{W}_{ki}\bar{\mathcal{V}}_{cj}^{ab}\right)\tilde{c}_k^c \\ &+ \left(\frac{1}{4}E_g\mathcal{W}_{ac}\mathcal{W}_{ki} + \frac{1}{2}\mathcal{W}_{ki}\tilde{\mathcal{F}}_{ac} - \frac{1}{2}\mathcal{W}_{ac}\tilde{\mathcal{F}}_{ki} + \bar{\mathcal{V}}_{ic}^{ak}\right)\mathcal{W}_{bd}\mathcal{W}_{lj}c_{kl}^c \\ &\left. + \left(\frac{1}{8}\mathcal{W}_{ac}\mathcal{W}_{bd}\bar{\mathcal{V}}_{ij}^{kl} + \frac{1}{8}\mathcal{W}_{ki}\mathcal{W}_{lj}\bar{\mathcal{V}}_{cd}^{ab} - \frac{1}{8}\mathcal{W}_{ai}\mathcal{W}_{bj}\bar{\mathcal{V}}_{cd}^{kl}\right)c_{kl}^c\right\}, \end{aligned} \quad (20c)$$

where  $\mathcal{P}$  is the permutation operator and the CI coefficients are factorized as

$$\tilde{c}_0 = c_0 + \mathcal{W}_{kc}c_k^c + \frac{1}{2}\mathcal{W}_{kc}\mathcal{W}_{ld}c_{kl}^{cd}, \quad (21)$$

$$\tilde{c}_k^c = c_k^c + \mathcal{W}_{ld}c_{kl}^{cd}. \quad (22)$$

For example,

$$\mathcal{N}_g = \tilde{d}_0\tilde{c}_0 + \tilde{d}_i^a\mathcal{W}_{ac}\tilde{c}_k^c\mathcal{W}_{ki} + \frac{1}{4}c_{ij}^{ab}\mathcal{W}_{ac}\mathcal{W}_{ki}\mathcal{W}_{bd}\mathcal{W}_{lj}c_{kl}^{cd}, \quad (23)$$

where we further define the renormalized CI coefficients of the bra state as

$$\tilde{d}_0 = c_0^* + c_i^{a*}\mathcal{W}_{ai} + \frac{1}{2}c_{ij}^{ab*}\mathcal{W}_{ai}\mathcal{W}_{bj}, \quad (24)$$

$$\tilde{d}_i^a = c_i^{a*} + c_{ij}^{ab*}\mathcal{W}_{bj}. \quad (25)$$

Note that we have omit subscript  $g$  for some of the matrices to improve the readability.

## 4 ECISD gradient

The orbital gradient of  $\mathcal{E}$  is shown to be

$$L_{pq} = \sum_g w_g n_g \left[ (\mathbf{P}_g)_{pq} (E_g - \mathcal{E}) + (\boldsymbol{\rho}_g)_{pq} (\mathcal{E}_g - E_g \mathcal{N}_g) - [\boldsymbol{\gamma}_g \mathbf{F}_g \boldsymbol{\rho}_g]_{pq} + [\boldsymbol{\eta}_g \mathbf{F}_g \mathbf{P}_g]_{pq} + [\boldsymbol{\eta}_g \mathcal{G}_g \boldsymbol{\rho}_g]_{pq} + (\boldsymbol{\zeta}_g)_{pq} - (\boldsymbol{\omega}_g)_{pi} \delta_{iq} + \delta_{pa} (\tilde{\boldsymbol{\omega}}_g)_{aq} \right], \quad (26)$$

with

$$(\mathbf{P}_g)_{pq} = \mathcal{N}_g (\boldsymbol{\rho}_g)_{pq} + (\boldsymbol{\gamma}_g)_{qp}, \quad (27)$$

$$(\mathcal{G}_g)_{pq} = \langle pr || qs \rangle (\boldsymbol{\gamma}_g)_{sr}, \quad (28)$$

$$\begin{aligned} (\boldsymbol{\gamma}_g)_{qp} &= \tilde{d}_0 \mathcal{R}_{qc} \tilde{c}_k^c \mathcal{L}_{kp} + \mathcal{R}_{qi} \tilde{d}_i^a \mathcal{L}_{ap} \tilde{c}_0 + \mathcal{R}_{qc} \tilde{c}_k^c \mathcal{W}_{ki} \tilde{d}_i^a \mathcal{L}_{ap} - \mathcal{R}_{qi} \tilde{d}_i^a \mathcal{W}_{ac} \tilde{c}_k^c \mathcal{L}_{kp} \\ &+ \mathcal{R}_{qd} c_{kl}^{cd} [\mathcal{W}_{ki} \tilde{d}_i^a \mathcal{W}_{ac}] \mathcal{L}_{lp} + \mathcal{R}_{qj} c_{ij}^{ab} [\mathcal{W}_{ac} \tilde{c}_k^c \mathcal{W}_{ki}] \mathcal{L}_{bp} \\ &+ \frac{1}{2} \left( \mathcal{R}_{qc} \mathcal{W}_{ki} \mathcal{L}_{ap} - \mathcal{R}_{qi} \mathcal{W}_{ac} \mathcal{L}_{kp} \right) \mathcal{W}_{bd} \mathcal{W}_{lj} c_{ij}^{ab} c_{kl}^{cd}, \end{aligned} \quad (29)$$

$$(\boldsymbol{\eta}_g)_{pq} = \delta_{pq} - (\boldsymbol{\rho}_g)_{pq}, \quad (30)$$

$$\begin{aligned} (\boldsymbol{\zeta}_g)_{pq} &= [\mathcal{R}_{pi} \tilde{d}_i^a \mathcal{L}_{aq}] \text{Tr}[\tilde{\mathcal{F}}_{kc} \tilde{c}_k^c] + [\mathcal{R}_{pc} \tilde{c}_k^c \mathcal{L}_{kq}] \text{Tr}[\tilde{\mathcal{F}}_{ai} \tilde{d}_i^a] \\ &- [\mathcal{R}_{pi} \tilde{d}_i^a \tilde{\mathcal{F}}_{ac} \tilde{c}_k^c \mathcal{L}_{kq}] - [\mathcal{R}_{pc} \tilde{c}_k^c \tilde{\mathcal{F}}_{ki} \tilde{d}_i^a \mathcal{L}_{aq}] + \mathcal{L}_{kq} \tilde{\mathcal{F}}_{ld} \mathcal{R}_{pc} \tilde{d}_0 c_{kl}^{cd} + \mathcal{L}_{aq} \tilde{\mathcal{F}}_{bj} \mathcal{R}_{pi} c_{ij}^{ab} \tilde{c}_0 \\ &+ \left( \mathcal{W}_{ki} \mathcal{L}_{aq} \tilde{\mathcal{F}}_{ld} \mathcal{R}_{pc} - \mathcal{W}_{ki} \tilde{\mathcal{F}}_{ad} \mathcal{L}_{lq} \mathcal{R}_{pc} - \mathcal{W}_{ac} \mathcal{L}_{kq} \tilde{\mathcal{F}}_{ld} \mathcal{R}_{pi} + \mathcal{W}_{ac} \mathcal{L}_{kq} \tilde{\mathcal{F}}_{li} \mathcal{R}_{pd} \right) \tilde{d}_i^a c_{kl}^{cd} \\ &+ \left( \mathcal{W}_{ac} \mathcal{L}_{bq} \tilde{\mathcal{F}}_{kj} \mathcal{R}_{pi} - \mathcal{W}_{ac} \tilde{\mathcal{F}}_{bj} \mathcal{L}_{kq} \mathcal{R}_{pi} + \mathcal{W}_{ki} \mathcal{L}_{aq} \tilde{\mathcal{F}}_{bj} \mathcal{R}_{pc} - \mathcal{W}_{ki} \mathcal{L}_{aq} \tilde{\mathcal{F}}_{bc} \mathcal{R}_{pj} \right) c_{ij}^{ab} \tilde{c}_k^c \\ &+ \left( \mathcal{W}_{bd} \mathcal{W}_{lj} \mathcal{L}_{aq} \tilde{\mathcal{F}}_{kc} \mathcal{R}_{pi} - \mathcal{W}_{bd} \mathcal{W}_{lj} \tilde{\mathcal{F}}_{ac} \mathcal{L}_{kq} \mathcal{R}_{pi} - \mathcal{W}_{bd} \mathcal{W}_{lj} \mathcal{L}_{aq} \tilde{\mathcal{F}}_{ki} \mathcal{R}_{pc} \right. \\ &+ \left. \mathcal{W}_{bd} \mathcal{W}_{lj} \tilde{\mathcal{F}}_{ai} \mathcal{L}_{kq} \mathcal{R}_{pc} + \frac{1}{2} \mathcal{W}_{ac} \mathcal{W}_{bd} \mathcal{L}_{kq} \mathcal{R}_{pi} \tilde{\mathcal{F}}_{lj} + \frac{1}{2} \mathcal{W}_{ki} \mathcal{W}_{lj} \mathcal{L}_{aq} \mathcal{R}_{pc} \tilde{\mathcal{F}}_{bd} \right) c_{ij}^{ab} c_{kl}^{cd} \\ &+ \left\{ -\mathcal{R}_{pj} \mathcal{L}_{bq} \bar{\mathcal{V}}_{ci}^{ak} + \frac{1}{4} \mathcal{R}_{pc} \mathcal{L}_{kq} \bar{\mathcal{V}}_{ij}^{ab} - \frac{1}{2} \mathcal{R}_{pc} \mathcal{L}_{bq} \bar{\mathcal{V}}_{ij}^{ak} + \frac{1}{2} \mathcal{R}_{pj} \mathcal{L}_{kq} \bar{\mathcal{V}}_{ci}^{ab} \right\} c_{ij}^{ab} \tilde{c}_k^c \\ &+ \left\{ -\mathcal{R}_{pd} \mathcal{L}_{lq} \bar{\mathcal{V}}_{ci}^{ak} + \frac{1}{4} \mathcal{R}_{pi} \mathcal{L}_{aq} \bar{\mathcal{V}}_{cd}^{kl} + \frac{1}{2} \mathcal{R}_{pi} \mathcal{L}_{lq} \bar{\mathcal{V}}_{cd}^{ak} - \frac{1}{2} \mathcal{R}_{pd} \mathcal{L}_{aq} \bar{\mathcal{V}}_{ci}^{kl} \right\} \tilde{d}_i^a c_{kl}^{cd} \\ &+ \left\{ \frac{1}{2} \mathcal{W}_{ki} \mathcal{R}_{pj} \mathcal{L}_{bq} \bar{\mathcal{V}}_{cd}^{al} + \frac{1}{2} \mathcal{W}_{bd} \mathcal{R}_{pj} \mathcal{L}_{aq} \bar{\mathcal{V}}_{ci}^{kl} + \frac{1}{2} \mathcal{W}_{bd} \mathcal{L}_{lq} \mathcal{R}_{pc} \bar{\mathcal{V}}_{ij}^{ak} + \frac{1}{2} \mathcal{W}_{lj} \mathcal{L}_{kq} \mathcal{R}_{pd} \bar{\mathcal{V}}_{ci}^{ab} \right. \\ &\left. - \mathcal{W}_{lj} \mathcal{L}_{bq} \mathcal{R}_{pd} \bar{\mathcal{V}}_{ci}^{ak} + \mathcal{W}_{bd} \mathcal{L}_{lq} \mathcal{R}_{pj} \bar{\mathcal{V}}_{ci}^{ak} + \frac{1}{4} \mathcal{L}_{aq} \mathcal{W}_{bd} \mathcal{R}_{pc} \bar{\mathcal{V}}_{ij}^{kl} - \frac{1}{4} \mathcal{W}_{lj} \mathcal{R}_{pi} \mathcal{L}_{kq} \bar{\mathcal{V}}_{cd}^{ab} \right\} c_{ij}^{ab} c_{kl}^{cd}, \end{aligned} \quad (31)$$

$$\begin{aligned}
(\omega_g)_{pq} &= \left( \bar{\mathcal{V}}_{qc}^{ak} \mathcal{R}_{pi} - \bar{\mathcal{V}}_{qi}^{ak} \mathcal{R}_{pc} \right) \tilde{d}_i^a \tilde{c}_k^c + \frac{1}{2} \bar{\mathcal{V}}_{qd}^{kl} \mathcal{R}_{pc} \tilde{d}_0^c c_{kl}^{cd} + \frac{1}{2} \bar{\mathcal{V}}_{qj}^{ab} \mathcal{R}_{pi} c_{ij}^{ab} \tilde{c}_0 \\
&+ \left( \mathcal{W}_{ki} \bar{\mathcal{V}}_{qd}^{al} \mathcal{R}_{pc} - \frac{1}{2} \mathcal{W}_{ac} \bar{\mathcal{V}}_{qd}^{kl} \mathcal{R}_{pi} + \frac{1}{2} \mathcal{W}_{ac} \bar{\mathcal{V}}_{qi}^{kl} \right) \tilde{d}_i^a c_{kl}^{cd} \\
&+ \left( \mathcal{W}_{ac} \bar{\mathcal{V}}_{qj}^{bk} \mathcal{R}_{pi} + \frac{1}{2} \mathcal{W}_{ki} \bar{\mathcal{V}}_{qj}^{ab} \mathcal{R}_{pc} - \frac{1}{2} \mathcal{W}_{ki} \bar{\mathcal{V}}_{qc}^{ab} \mathcal{R}_{pj} \right) c_{ij}^{ab} \tilde{c}_k^c \\
&+ \left( \mathcal{W}_{bd} \mathcal{W}_{lj} \bar{\mathcal{V}}_{qc}^{ak} \mathcal{R}_{pi} - \mathcal{W}_{bd} \mathcal{W}_{lj} \bar{\mathcal{V}}_{qi}^{ak} \mathcal{R}_{pc} + \frac{1}{4} \mathcal{W}_{ac} \mathcal{W}_{bd} \bar{\mathcal{V}}_{qj}^{kl} \mathcal{R}_{pi} + \frac{1}{4} \mathcal{W}_{ki} \mathcal{W}_{lj} \bar{\mathcal{V}}_{qd}^{ab} \mathcal{R}_{pc} \right) c_{ij}^{ab} c_{kl}^{cd},
\end{aligned} \tag{32}$$

$$\begin{aligned}
(\tilde{\omega}_g)_{pq} &= \left( \mathcal{L}_{aq} \bar{\mathcal{V}}_{ic}^{pk} - \mathcal{L}_{kq} \bar{\mathcal{V}}_{ic}^{pa} \right) \tilde{d}_i^a \tilde{c}_k^c + \frac{1}{2} \mathcal{L}_{kq} \bar{\mathcal{V}}_{cd}^{pl} \tilde{d}_0^c c_{kl}^{cd} + \frac{1}{2} \mathcal{L}_{aq} \bar{\mathcal{V}}_{ij}^{pb} c_{ij}^{ab} \tilde{c}_0 \\
&+ \left( \frac{1}{2} \mathcal{W}_{ki} \mathcal{L}_{aq} \bar{\mathcal{V}}_{cd}^{pl} - \frac{1}{2} \mathcal{W}_{ki} \mathcal{L}_{lq} \bar{\mathcal{V}}_{cd}^{pa} - \mathcal{W}_{ac} \mathcal{L}_{kq} \bar{\mathcal{V}}_{id}^{pl} \right) \tilde{d}_i^a c_{kl}^{cd} \\
&+ \left( \frac{1}{2} \mathcal{W}_{ac} \mathcal{L}_{bq} \bar{\mathcal{V}}_{ij}^{pk} - \frac{1}{2} \mathcal{W}_{ac} \mathcal{L}_{kq} \bar{\mathcal{V}}_{ij}^{pb} + \mathcal{W}_{ki} \mathcal{L}_{aq} \bar{\mathcal{V}}_{cj}^{pb} \right) c_{ij}^{ab} \tilde{c}_k^c \\
&+ \left( \mathcal{W}_{bd} \mathcal{W}_{lj} \mathcal{L}_{aq} \bar{\mathcal{V}}_{ic}^{pk} - \mathcal{W}_{bd} \mathcal{W}_{lj} \mathcal{L}_{kq} \bar{\mathcal{V}}_{ic}^{pa} + \frac{1}{4} \mathcal{W}_{ac} \mathcal{W}_{bd} \mathcal{L}_{kq} \bar{\mathcal{V}}_{ij}^{pl} + \frac{1}{4} \mathcal{W}_{ki} \mathcal{W}_{lj} \mathcal{L}_{aq} \bar{\mathcal{V}}_{cd}^{pb} \right) c_{ij}^{ab} c_{kl}^{cd}.
\end{aligned} \tag{33}$$

## 5 ECEPA

The energy derivative with respect to  $x$  is generally written as

$$F^x = h_{\mu\nu}^x P_{\nu\mu}^{\text{rel}} + \frac{1}{4} \langle \mu\nu || \lambda\sigma \rangle^x P_{\nu\mu,\sigma\lambda}^{\text{rel}} + S_{\mu\nu}^x W_{\nu\mu}. \tag{34}$$

The relaxed density matrices are given by

$$\mathbf{P}^{\text{rel}} = \mathbf{P} + \mathbf{P}^{\text{corr}}, \tag{35}$$

both for one-particle and two-particle components. The unrelaxed part for ECEPA is

$$\mathbf{P} = \sum_g w_g n_g \left[ (1 - \alpha) \boldsymbol{\rho}_g + \alpha \mathbf{P}_g \right], \tag{36}$$

where

$$\alpha = \frac{1}{1 - \zeta \langle \Psi | \hat{\mathcal{P}} \hat{\mathcal{Q}} | \Psi \rangle} \quad (37)$$

is a scaling factor. Eq.(36) is also true for the unrelaxed two-particle density matrix; one is to replace  $\boldsymbol{\rho}_g$  with the two-particle transition density matrix of SUHF and  $\mathbf{P}_g$  with that of ECISD,

$$(\mathbf{P}_g)_{pq,rs} = \mathcal{P}(pq)\mathcal{P}(rs) \left( \frac{1}{2} \mathcal{N}_g(\boldsymbol{\rho}_g)_{rp}(\boldsymbol{\rho}_g)_{sq} + (\boldsymbol{\gamma}_g)_{rp}(\boldsymbol{\rho}_g)_{sq} \right) + \langle \Psi | \{a_p^\dagger a_q^\dagger a_s a_r\} | \Psi_g \rangle \quad (38)$$

where

$$\begin{aligned} \langle \Psi | \{a_p^\dagger a_q^\dagger a_s a_r\} | \Psi_g \rangle = & \mathcal{P}(pq)\mathcal{P}(rs) \left\{ \mathcal{L}_{ap} \mathcal{L}_{kq} \mathcal{R}_{ri} \mathcal{R}_{sc} \tilde{d}_i^a \tilde{c}_k^c + \frac{1}{4} \mathcal{L}_{kp} \mathcal{L}_{lq} \mathcal{R}_{rc} \mathcal{R}_{sd} \tilde{d}_0^c c_{kl}^{cd} \right. \\ & + \frac{1}{4} \mathcal{L}_{ap} \mathcal{L}_{bq} \mathcal{R}_{ri} \mathcal{R}_{sj} c_{ij}^{ab} \tilde{c}_0 \\ & + \frac{1}{2} (\mathcal{W}_{ki} \mathcal{L}_{ap} \mathcal{L}_{lq} \mathcal{R}_{rc} \mathcal{R}_{sd} - \mathcal{W}_{ac} \mathcal{L}_{kp} \mathcal{L}_{lq} \mathcal{R}_{ri} \mathcal{R}_{sd}) \tilde{d}_i^a c_{kl}^{cd} \\ & + \frac{1}{2} (\mathcal{W}_{ac} \mathcal{L}_{bp} \mathcal{L}_{kq} \mathcal{R}_{ri} \mathcal{R}_{sj} c_{ij}^{ab} + \mathcal{W}_{ki} \mathcal{L}_{ap} \mathcal{L}_{bq} \mathcal{R}_{rc} \mathcal{R}_{sj}) c_{ij}^{ab} \tilde{c}_k^c \\ & + \left( \mathcal{W}_{bd} \mathcal{W}_{lj} \mathcal{L}_{ap} \mathcal{L}_{kq} \mathcal{R}_{ri} \mathcal{R}_{sc} + \frac{1}{8} \mathcal{W}_{ac} \mathcal{W}_{bd} \mathcal{L}_{kp} \mathcal{L}_{lq} \mathcal{R}_{ri} \mathcal{R}_{sj} \right. \\ & \left. + \frac{1}{8} \mathcal{W}_{ki} \mathcal{W}_{lj} \mathcal{L}_{ap} \mathcal{L}_{bq} \mathcal{R}_{rc} \mathcal{R}_{sd} \right) c_{ij}^{ab} c_{kl}^{cd} \left. \right\}. \quad (39) \end{aligned}$$

The relaxation correction for the one-particle density matrix is given by

$$\begin{aligned} \mathbf{P}^{\text{corr}} = & \sum_g w_g n_g (\mathbf{P}_g^{\text{corr}})_{pq} \\ = & \sum_g w_g n_g \left\{ (\boldsymbol{\rho}_g)_{pq} \left( (\mathcal{W}_g)_{ia} - N_{ia} + (\mathcal{W}_g)_{ai} - N_{ai} \right) z_{ia} \right. \\ & \left. + (\mathcal{R}_g)_{pi} z_{ia} (\mathcal{L}_g)_{aq} + (\mathcal{R}_g)_{pa} z_{ai} (\mathcal{L}_g)_{iq} \right\}, \quad (40) \end{aligned}$$



where

$$N_{ai} = N_{ia} = \sum_g w_g n_g \mathcal{W}_{ai}, \quad (41)$$

and  $\mathbf{z}$  are the solution of coupled-perturbed PHF equation with the ECEPA orbital Lagrangian  $\tilde{\mathbf{L}}$ ,

$$\tilde{L}_{pq} = \alpha (L_{pq} + \zeta E_c \xi_{pq}). \quad (42)$$

The relaxation correction to the two-particle part can be similarly obtained as

$$\begin{aligned} P_{qp,sr}^{\text{corr}} = \sum_g w_g n_g & \left[ 4 \left( (\mathcal{R}_g)_{ra} z_{ai} (\mathcal{L}_g)_{ip} + (\mathcal{R}_g)_{ri} z_{ia} (\mathcal{L}_g)_{ap} \right) (\boldsymbol{\rho}_g)_{sq} \right. \\ & \left. + 2 (\boldsymbol{\rho}_g)_{rp} (\boldsymbol{\rho}_g)_{sq} \left( (\mathcal{W}_g)_{ia} - N_{ia} + (\mathcal{W}_g)_{ai} - N_{ai} \right) z_{ai} \right]. \end{aligned} \quad (43)$$

Finally, the energy-weighted density matrix is also represented as a mixture of SUHF and ECISD contributions,

$$\begin{aligned} W_{pq} = - \sum_g w_g n_g & \left[ (\mathbf{F}_g)_{pr} \left( (1 - \alpha) \boldsymbol{\rho}_g + \alpha \mathbf{P}_g + \mathbf{P}_g^{\text{corr}} \right)_{rq} \right. \\ & \left. + \langle pr || us \rangle (\boldsymbol{\rho}_g)_{uq} \left( (\mathcal{R}_g)_{sa} z_{ai} (\mathcal{L}_g)_{ir} + (\mathcal{R}_g)_{si} z_{ia} (\mathcal{L}_g)_{ar} \right) + \alpha [\mathcal{G}_g \boldsymbol{\rho}_g]_{pq} + \alpha [\mathcal{L}_g^{-1} \tilde{\boldsymbol{\omega}}_g]_{pq} \right]. \end{aligned} \quad (44)$$

## 6 The geometries and total energies of the benchmark molecules for singlet-triplet splittings

C	Energy			$T_e$	
	Singlet	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )
SUHF	-37.662 017	-37.698 887	-37.697 584	23.1	22.3
ECISD	-37.737 946	-37.784 653	-37.784 519	29.3	29.2
ECISD+Q	-37.741 147	-37.788 795	-37.788 650	29.9	29.8
ELCC	-37.741 545	-37.789 371	-37.789 218	30.0	29.9
EACPF	-37.739 638	-37.786 855	-37.786 714	29.6	29.5
EAQCC	-37.738 490	-37.785 357	-37.785 222	29.4	29.3
EAQCCh	-37.738 882	-37.785 867	-37.785 730	29.5	29.4
CCSD	-37.729 908		-37.784 472		34.2
CCSD(T)	-37.735 505		-37.786 875		32.2
UCCSD(T)	-37.774 802		-37.786 875		7.6
Exp.				29.1	29.1

O	Energy			$T_e$	
	Singlet	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )
SUHF	-74.762 052	-74.822 032	-74.823 730	37.6	38.7
ECISD	-74.916 973	-74.988 765	-74.989 082	45.1	45.2
ECISD+Q	-74.921 927	-74.994 820	-74.994 809	45.7	45.7
ELCC	-74.922 397	-74.995 508	-74.995 374	45.9	45.8
EACPF	-74.920 474	-74.993 088	-74.993 139	45.6	45.6
EAQCC	-74.919 024	-74.991 285	-74.991 456	45.3	45.5
EAQCCh	-74.919 523	-74.991 905	-74.992 035	45.4	45.5
CCSD	-74.903 851		-74.991 398		54.9
CCSD(T)	-74.915 104		-74.995 267		50.3
UCCSD(T)	-74.976 666		-74.995 267		11.7
Exp.				45.4	45.4

Si	Energy			$T_e$	
	Singlet	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )
SUHF	-288.848 617	-288.865 963	-288.861 886	10.9	8.3
ECISD	-288.935 539	-288.963 161	-288.962 787	17.3	17.1
ECISD+Q	-288.940 054	-288.969 208	-288.969 042	18.3	18.2
ELCC	-288.940 868	-288.970 498	-288.970 306	18.6	18.5
EACPF	-288.939 646	-288.968 775	-288.968 558	18.3	18.1
EAQCC	-288.938 635	-288.967 368	-288.967 122	18.0	17.9
EAQCCh	-288.938 982	-288.967 855	-288.967 613	18.1	18.0
CCSD	-288.930 020		-288.964 120	21.4	
CCSD(T)	-288.936 439		-288.967 676	19.6	
UCCSD(T)	-288.957 866		-288.967 676	6.2	
Exp.				17.3	17.3

NH	Energy			$T_e$	
	Singlet	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )
SUHF	-55.191 361	-55.236 954	-55.248 818	28.6	36.1
ECISD	-55.090 906	-55.147 865	-55.148 747	35.7	36.3
ECISD+Q	-55.097 450	-55.155 628	-55.156 006	36.5	36.7
ELCC	-55.098 317	-55.156 758	-55.157 042	36.7	36.9
EACPF	-55.095 627	-55.153 507	-55.154 014	36.3	36.6
EAQCC	-55.093 646	-55.151 130	-55.151 797	36.1	36.5
EAQCCh	-55.094 324	-55.151 942	-55.152 554	36.2	36.5
CCSD	-55.077 839		-55.151 513		46.2
CCSD(T)	-55.087 363		-55.156 141		43.2
UCCSD(T)	-55.140 179		-55.156 141		10.0
Exp.				35.9	35.9

OH <sup>+</sup>	Energy			$T_e$	
	Singlet	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )
SUHF	-74.946 173	-75.011 534	-75.018 107	41.0	45.1
ECISD	-75.101 898	-75.180 861	-75.181 604	49.5	50.0
ECISD+Q	-75.106 893	-75.187 264	-75.187 379	50.4	50.5
ELCC	-75.107 338	-75.187 994	-75.187 986	50.6	50.6
EACPF	-75.105 417	-75.185 436	-75.185 710	50.2	50.4
EAQCC	-75.103 962	-75.183 528	-75.184 003	49.9	50.2
EAQCCh	-75.104 464	-75.184 183	-75.184 589	50.0	50.3
CCSD	-75.084 500		-75.183 797		62.3
CCSD(T)	-75.095 529		-75.187 429		57.7
UCCSD(T)	-75.169 520		-75.187 429		11.2
Exp.				50.5	50.5

O <sub>2</sub>	Energy			T <sub>e</sub>	
	Singlet	Triplet (m <sub>s</sub> = 0)	Triplet (m <sub>s</sub> = 1)	Triplet (m <sub>s</sub> = 0)	Triplet (m <sub>s</sub> = 1)
SUHF	-149.667 484	-149.682 976	-149.688 163	9.7	13.0
ECISD	-150.079 271	-150.115 317	-150.128 695	22.6	31.0
ECISD+Q	-150.115 766	-150.152 625	-150.161 973	23.1	29.0
ELCC	-150.130 234	-150.164 653	-150.171 730	21.6	26.0
EACPF	-150.118 577	-150.154 024	-150.162 672	22.2	27.7
EAQCC	-150.109 584	-150.145 491	-150.155 302	22.5	28.7
EAQCCh	-150.112 593	-150.148 380	-150.157 801	22.5	28.4
CCSD	-150.105 964		-150.158 049		32.7
CCSD(T)	-150.131 661		-150.178 680		29.5
UCCSD(T)	-150.162 228		-150.178 680		10.3
Exp.				22.6	22.6

NF	Energy			T <sub>e</sub>	
	Singlet	Triplet (m <sub>s</sub> = 0)	Triplet (m <sub>s</sub> = 1)	Triplet (m <sub>s</sub> = 0)	Triplet (m <sub>s</sub> = 1)
SUHF	-153.809 001	-153.850 578	-153.859 322	26.1	31.6
ECISD	-154.192 453	-154.238 490	-154.257 497	28.9	40.8
ECISD+Q	-154.219 614	-154.266 949	-154.286 795	29.7	42.2
ELCC	-154.229 576	-154.277 217	-154.294 272	29.9	40.6
EACPF	-154.220 863	-154.268 310	-154.286 758	29.8	41.3
EAQCC	-154.214 418	-154.261 574	-154.280 539	29.6	41.5
EAQCCh	-154.216 565	-154.263 825	-154.282 657	29.7	41.5
CCSD	-154.212 348		-154.282 471		44.0
CCSD(T)	-154.233 779		-154.298 764		40.8
UCCSD(T)	-154.281 275		-154.298 764		11.0
Exp.				34.3	34.3

CH <sub>2</sub>	Energy			T <sub>e</sub>	
	Singlet	Triplet (m <sub>s</sub> = 0)	Triplet (m <sub>s</sub> = 1)	Triplet (m <sub>s</sub> = 0)	Triplet (m <sub>s</sub> = 1)
SUHF	-38.928 368	-38.940 187	-38.946 313	7.4	11.3
ECISD	-39.066 272	-39.080 808	-39.081 411	9.1	9.5
ECISD+Q	-39.074 463	-39.087 921	-39.087 891	8.4	8.4
ELCC	-39.076 595	-39.088 978	-39.088 794	7.8	7.7
EACPF	-39.072 530	-39.085 986	-39.086 105	8.4	8.5
EAQCC	-39.069 805	-39.083 802	-39.084 131	8.8	9.0
EAQCCh	-39.070 717	-39.084 548	-39.084 806	8.7	8.8
CCSD	-39.067 547		-39.084 141		10.4
CCSD(T)	-39.073 004		-39.088 071		9.5
UCCSD(T)	-39.072 764		-39.088 071		9.6
Exp.				9.0	9.0

NH <sup>+</sup>	Energy			$T_e$	
	Singlet	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )
SUHF	-54.940 895	-54.987 628	-54.993 056	29.3	32.7
ECISD	-55.349 056	-55.394 775	-55.395 967	28.7	29.4
ECISD+Q	-55.356 630	-55.401 808	-55.401 777	28.3	28.3
ELCC	-55.360 034	-55.402 728	-55.402 430	26.8	26.6
EACPF	-55.355 029	-55.399 847	-55.400 115	28.1	28.3
EAQCC	-55.352 353	-55.397 720	-55.398 386	28.5	28.9
EAQCCh	-55.353 227	-55.398 448	-55.398 979	28.4	28.7
CCSD	-55.349 992		-55.398 201		30.3
CCSD(T)	-55.355 502		-55.401 862		29.1
UCCSD(T)	-55.366 988		-55.401 862		21.9
Exp.				29.0	29.0

SiH <sub>2</sub>	Energy			$T_e$	
	Singlet	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )
SUHF	-290.062 035	-290.029 621	-290.029 647	-20.3	-20.3
ECISD	-290.204 493	-290.171 045	-290.170 737	-21.0	-21.2
ECISD+Q	-290.214 336	-290.179 937	-290.179 551	-21.6	-21.8
ELCC	-290.202 756	-290.169 760	-290.181 369	-20.7	-13.4
EACPF	-290.214 359	-290.179 735	-290.179 283	-21.7	-22.0
EAQCC	-290.212 255	-290.177 923	-290.177 517	-21.5	-21.8
EAQCCh	-290.212 972	-290.178 543	-290.178 122	-21.6	-21.9
CCSD	-290.208 461		-290.176 265		-20.2
CCSD(T)	-290.213 590		-290.180 655		-20.7
UCCSD(T)	-290.213 241		-290.180 655		-20.4
Exp.				-21.0	-21.0

PH <sup>+</sup>	Energy			$T_e$	
	Singlet	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )
SUHF	-341.575 519	-341.550 969	-341.551 034	-15.4	-15.4
ECISD	-341.738 499	-341.709 708	-341.709 261	-18.1	-18.3
ECISD+Q	-341.749 634	-341.719 287	-341.718 770	-19.0	-19.4
ELCC	-341.736 244	-341.708 464	-341.720 597	-17.4	-9.8
EACPF	-341.749 774	-341.718 972	-341.718 398	-19.3	-19.7
EAQCC	-341.747 341	-341.717 060	-341.716 526	-19.0	-19.3
EAQCCh	-341.748 167	-341.717 715	-341.717 168	-19.1	-19.5
CCSD	-341.741 839		-341.713 412		-17.8
CCSD(T)	-341.747 446		-341.718 337		-18.3
UCCSD(T)	-341.747 010		-341.718 337		-18.0
Exp.				-17.0	-17.0

CF <sub>2</sub>	Energy			$T_e$	
	Singlet	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )
SUHF	-236.824 432	-236.725 385	-236.728 476	-62.2	-60.2
ECISD	-237.418 319	-237.323 998	-237.330 096	-59.2	-55.4
ECISD+Q	-237.474 705	-237.377 395	-237.383 683	-61.1	-57.1
ELCC	-237.497 056	-237.395 732	-237.400 053	-63.6	-60.9
EACPF	-237.484 568	-237.384 782	-237.389 941	-62.6	-59.4
EAQCC	-237.474 241	-237.375 587	-237.381 183	-61.9	-58.4
EAQCCh	-237.477 733	-237.378 727	-237.384 174	-62.1	-58.7
CCSD	-237.473 747		-237.387 010		-54.4
CCSD(T)	-237.500 344		-237.410 082		-56.6
UCCSD(T)	-237.500 081		-237.410 082		-56.5
Exp.				-56.6	-56.6

H <sub>2</sub> CC	Energy			$T_e$	
	Singlet	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )	Triplet ( $m_s = 0$ )	Triplet ( $m_s = 1$ )
SUHF	-76.849 525	-76.751 847	-76.746 814	-61.3	-64.5
ECISD	-77.111 066	-77.029 642	-77.012 275	-51.1	-62.0
ECISD+Q	-77.134 816	-77.056 599	-77.037 320	-49.1	-61.2
ELCC	-77.143 989	-77.069 628	-77.054 593	-46.7	-56.1
EACPF	-77.135 164	-77.058 009	-77.040 155	-48.4	-59.6
EAQCC	-77.128 632	-77.050 024	-77.031 783	-49.3	-60.8
EAQCCh	-77.130 810	-77.052 650	-77.034 456	-49.0	-60.5
CCSD	-77.124 009		-77.051 453		-45.5
CCSD(T)	-77.139 669		-77.065 103		-46.8
UCCSD(T)	-77.139 457		-77.065 103		-46.7
Exp.				-48.6	-48.6

## 7 The raw energies of Cr<sub>2</sub> for each basis set.

Table 1: Cr<sub>2</sub>/cc-pVDZ.

<i>R</i>	SUHF	ECISD	ECISD+Q	EAQCC	EAQCCh	EACPF
1.40	-2086.302 279	-2086.928 448	-2087.027 380	-2087.155 506	-2087.198 510	—
1.45	-2086.367 608	-2086.973 956	-2087.068 588	-2087.186 364	-2087.224 581	—
1.50	-2086.420 778	-2087.008 519	-2087.098 351	-2087.203 139	-2087.235 617	—
1.55	-2086.464 412	-2087.035 219	-2087.120 102	-2087.211 911	-2087.239 126	—
1.60	-2086.500 488	-2087.056 204	-2087.136 248	-2087.216 026	-2087.238 867	-2087.310 648
1.67	-2086.541 127	-2087.078 813	-2087.152 619	-2087.217 514	-2087.235 572	-2087.288 926
1.70	-2086.555 720	-2087.086 707	-2087.158 093	-2087.217 310	-2087.233 697	-2087.281 089
1.80	-2086.595 135	-2087.107 619	-2087.172 148	-2087.215 395	-2087.227 321	-2087.260 048
1.90	-2086.624 119	-2087.122 839	-2087.182 242	-2087.213 764	-2087.222 612	-2087.245 777
2.00	-2086.646 005	-2087.134 393	-2087.190 059	-2087.213 402	-2087.220 163	-2087.237 074
2.10	-2086.662 844	-2087.143 321	-2087.196 265	-2087.214 095	-2087.219 488	-2087.232 384
2.20	-2086.675 927	-2087.150 172	-2087.201 101	-2087.215 263	-2087.219 766	-2087.230 125
2.30	-2086.686 106	-2087.155 273	-2087.204 666	-2087.216 371	-2087.220 301	-2087.229 043
2.40	-2086.693 980	-2087.158 873	-2087.207 046	-2087.217 063	-2087.220 603	-2087.228 307
2.50	-2086.700 001	-2087.161 192	-2087.208 357	-2087.217 169	-2087.220 445	-2087.227 444
2.60	-2086.704 533	-2087.162 448	-2087.208 748	-2087.216 655	-2087.219 731	-2087.226 239
2.70	-2086.707 872	-2087.162 847	-2087.208 382	-2087.215 575	-2087.218 498	-2087.224 633
2.80	-2086.710 267	-2087.162 582	-2087.207 427	-2087.214 026	-2087.216 824	-2087.222 659
2.90	-2086.711 923	-2087.161 823	-2087.206 037	-2087.212 123	-2087.214 813	-2087.220 392
3.00	-2086.713 009	-2087.160 719	-2087.204 351	-2087.209 981	-2087.212 574	-2087.217 926
3.10	-2086.713 662	-2087.159 392	-2087.202 487	-2087.207 703	-2087.210 208	-2087.215 353
3.20	-2086.713 994	-2087.157 942	-2087.200 543	-2087.205 381	-2087.207 805	-2087.212 759
3.30	-2086.714 093	-2087.156 445	-2087.198 595	-2087.203 085	-2087.205 435	-2087.210 213
3.40	-2086.714 028	-2087.154 960	-2087.196 697	-2087.200 869	-2087.203 152	-2087.207 767
3.50	-2086.713 851	-2087.153 525	-2087.194 889	-2087.198 769	-2087.200 992	-2087.205 459
100.00	-2086.709 998	-2087.141 291	-2087.179 746	-2087.181 391	-2087.183 165	-2087.186 600

Table 2: Cr<sub>2</sub>/cc-pVTZ.

<i>R</i>	SUHF	ECISD	ECISD+Q	EAQCC	EAQCCch	EACPF
1.40	-2086.316 400	-2087.113 026	-2087.227 310	-2087.360 532	-2087.409 885	—
1.45	-2086.378 924	-2087.141 337	-2087.256 920	-2087.403 873	-2087.432 553	—
1.50	-2086.429 930	-2087.189 119	-2087.293 934	-2087.403 920	-2087.441 551	—
1.55	-2086.471 897	-2087.215 265	-2087.315 163	-2087.412 168	-2087.443 993	—
1.60	-2086.506 690	-2087.236 340	-2087.331 554	-2087.416 344	-2087.443 322	—
1.67	-2086.546 008	-2087.259 770	-2087.349 096	-2087.418 521	-2087.440 104	-2087.509 692
1.70	-2086.560 161	-2087.268 180	-2087.355 267	-2087.418 778	-2087.438 435	-2087.500 398
1.80	-2086.598 491	-2087.291 220	-2087.372 101	-2087.418 913	-2087.433 407	-2087.476 333
1.90	-2086.626 783	-2087.308 740	-2087.385 101	-2087.419 668	-2087.430 540	-2087.460 911
2.00	-2086.648 217	-2087.322 486	-2087.395 607	-2087.421 657	-2087.430 081	-2087.452 215
2.10	-2086.664 760	-2087.333 362	-2087.404 137	-2087.424 441	-2087.431 268	-2087.448 168
2.20	-2086.677 648	-2087.341 888	-2087.410 919	-2087.427 379	-2087.433 177	-2087.446 816
2.30	-2086.687 694	-2087.348 417	-2087.416 098	-2087.429 955	-2087.435 084	-2087.446 685
2.40	-2086.695 479	-2087.353 233	-2087.419 823	-2087.431 864	-2087.436 547	-2087.446 842
2.50	-2086.701 442	-2087.356 598	-2087.422 269	-2087.432 991	-2087.437 362	-2087.446 784
2.60	-2086.705 936	-2087.358 763	-2087.423 632	-2087.433 349	-2087.437 491	-2087.446 298
2.70	-2086.709 253	-2087.359 965	-2087.424 118	-2087.433 033	-2087.436 996	-2087.445 339
2.80	-2086.711 634	-2087.360 418	-2087.423 920	-2087.432 168	-2087.435 984	-2087.443 957
2.90	-2086.713 282	-2087.360 311	-2087.423 217	-2087.430 891	-2087.434 582	-2087.442 243
3.00	-2086.714 362	-2087.359 807	-2087.422 169	-2087.429 335	-2087.432 915	-2087.440 299
3.10	-2086.715 011	-2087.359 024	-2087.420 884	-2087.427 596	-2087.431 078	-2087.438 223
3.20	-2086.715 339	-2087.358 078	-2087.419 481	-2087.425 781	-2087.429 175	-2087.436 099
3.30	-2086.715 433	-2087.357 045	-2087.418 034	-2087.423 959	-2087.427 273	-2087.433 997
3.40	-2086.715 364	-2087.355 989	-2087.416 604	-2087.422 188	-2087.425 429	-2087.431 969
3.50	-2086.715 184	-2087.354 944	-2087.415 223	-2087.420 499	-2087.423 675	-2087.430 053
100.00	-2086.711 364	-2087.345 563	-2087.403 342	-2087.406 267	-2087.408 979	-2087.414 253



Table 3: Cr<sub>2</sub>/cc-pVQZ.

<i>R</i>	SUHF	ECISD	ECISD+Q	EAQCC	EAQCCh	EACPF
1.40	-2086.321 550	-2087.197 019	-2087.318 709	-2087.453 819	-2087.505 386	—
1.45	-2086.383 370	-2087.239 103	-2087.356 226	-2087.480 905	-2087.527 224	—
1.50	-2086.433 784	-2087.271 572	-2087.383 744	-2087.495 664	-2087.535 447	—
1.55	-2086.475 256	-2087.297 176	-2087.404 432	-2087.503 432	-2087.537 137	—
1.60	-2086.509 639	-2087.317 806	-2087.420 410	-2087.507 169	-2087.535 892	—
1.67	-2086.548 511	-2087.340 745	-2087.436 643	-2087.508 818	-2087.531 874	-2087.609 069
1.70	-2086.562 513	-2087.348 993	-2087.443 600	-2087.508 899	-2087.529 939	-2087.598 671
1.80	-2086.600 480	-2087.371 592	-2087.460 137	-2087.508 584	-2087.524 178	-2087.571 814
1.90	-2086.628 565	-2087.388 849	-2087.473 009	-2087.509 131	-2087.520 894	-2087.554 617
2.00	-2086.649 880	-2087.402 369	-2087.483 383	-2087.510 956	-2087.520 150	-2087.544 786
2.10	-2086.666 345	-2087.413 021	-2087.491 746	-2087.513 555	-2087.521 074	-2087.539 969
2.20	-2086.679 170	-2087.421 335	-2087.498 348	-2087.516 289	-2087.522 724	-2087.538 043
2.30	-2086.689 160	-2087.427 658	-2087.503 336	-2087.518 641	-2087.524 371	-2087.537 456
2.40	-2086.696 892	-2087.432 292	-2087.506 882	-2087.520 335	-2087.525 591	-2087.537 244
2.50	-2086.702 809	-2087.435 515	-2087.509 185	-2087.521 277	-2087.526 201	-2087.536 894
2.60	-2086.707 266	-2087.437 573	-2087.510 433	-2087.521 492	-2087.526 170	-2087.536 183
2.70	-2086.710 554	-2087.438 708	-2087.510 844	-2087.521 069	-2087.525 556	-2087.535 058
2.80	-2086.712 916	-2087.439 125	-2087.510 600	-2087.520 130	-2087.524 459	-2087.533 552
2.90	-2086.714 551	-2087.438 999	-2087.509 869	-2087.518 797	-2087.522 992	-2087.531 741
3.00	-2086.715 624	-2087.438 484	-2087.508 799	-2087.517 193	-2087.521 270	-2087.529 714
3.10	-2086.716 269	-2087.437 689	-2087.507 488	-2087.515 406	-2087.519 377	-2087.527 557
3.20	-2086.716 597	-2087.436 726	-2087.506 055	-2087.513 537	-2087.517 413	-2087.525 351
3.30	-2086.716 692	-2087.435 668	-2087.504 567	-2087.511 654	-2087.515 433	-2087.523 160
3.40	-2086.716 623	-2087.434 573	-2087.503 082	-2087.509 809	-2087.513 519	-2087.521 037
3.50	-2086.716 444	-2087.433 487	-2087.501 642	-2087.508 042	-2087.511 683	-2087.519 021
100.00	-2086.712 641	-2087.423 763	-2087.489 345	-2087.493 304	-2087.496 451	-2087.502 594