A Lagrangian, integral-density direct formulation and implementation of the analytic CCSD and CCSD(T) gradients

Kasper Hald, Asger Halkier, and Poul Jørgensen
Department of Chemistry, University of Århus, DK-8000 Århus C, Denmark

Sonia Coriani[a)]
Dipartimento di Scienze Chimiche, Università degli Studi di Trieste via Licio Giorgieri 1, I-34127 Trieste, Italy

Christof Hättig
Forschungszentrum Karlsruhe, Institute of Nanotechnology, P.O. Box 3640, D-76021 Karlsruhe, Germany

Trygve Helgaker
Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Norway

(Received 5 August 2002; accepted 29 October 2002)

Using a Lagrangian formulation an integral-density direct implementation of the analytic CCSD(T) molecular gradient is presented, which circumvents the bottleneck of storing either $\mathcal{O}(N^4)$ two-electron integrals or $\mathcal{O}(N^4)$ density matrix elements on disk. Canonical orbitals are used to simplify the implementation of the frozen-core approximation and the CCSD gradient is obtained as a special case. Also a new, simplified approach to (geometrical) derivative integrals is presented. As a first application we report a full geometry optimization for the most stable isomer of SiC_3 using the cc-pV5Z basis set with 368 contracted basis functions and the frozen-core approximation. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1531106]

I. INTRODUCTION

Many important molecular properties may be evaluated from derivatives of the electronic energy with respect to a given perturbation. Among the properties derived from the first energy derivatives are expectation values, in particular the molecular electric dipole and quadrupole moments, which characterize the charge distribution in the molecule. Within the Born-Oppenheimer approximation, the electronic energy represents the potential for the motion of the nuclei and the equilibrium geometry of a molecule is given by the minimum of the electronic energy with respect to the nuclear coordinates. Efficient optimizations of molecular equilibrium geometries thus rely on the implementation of analytic gradients. Geometry optimizations are indeed one of the most common tasks in computational chemistry, and accurate geometries are of fundamental importance to obtain accurate molecular properties. Also, harmonic vibrational frequencies and dipole gradients, needed to simulate the infra-red spectrum of a molecule within the double harmonic approximation, may be obtained by numerical differentiation of, respectively, the gradient and the dipole moment with respect to the nuclear coordinates.

The detailed theory behind the computation of analytical energy derivatives is well-known for conventional electronic wave functions (see Refs. 1, 2 for reviews), and different implementations of first and second derivatives have been presented.[3–14] Especially important are the implementations concerning the hierarchy of wave functions second-order Møller–Plesset perturbation theory (MP2), coupled-cluster singles-and-doubles (CCSD) and CCSD augmented with a perturbational correction for connected triple excitations [CCSD(T)], which offers a systematic improvement in the description of correlation effects at each level.

Beyond the density functional theory (DFT) and MP2 levels, the coupled-cluster (CC) approach is presently recognized as the most efficient way of describing dynamical correlation for systems with wave functions dominated by a single determinant. With the progress in integral-direct techniques[15–17] the application range of CC theory has increased significantly, allowing us to treat systems that only a few years ago were too large. The CCSD model, defined upon restriction of the cluster operator to single and double excitations, is the simplest and most commonly used model in the CC hierarchy and has a computational scaling of $\mathcal{O}(O^2V^4)$, where O and V are the number of occupied and virtual orbitals in the Hartree–Fock (HF) determinant, respectively.[18] Truncation at the triple excitation level results in the CCSDT model,[19–21] which scales as $\mathcal{O}(O^3V^5)$ and $\mathcal{O}(O^4V^4)$ and is too demanding for routine applications. However, it has been recognized that triple excitations are mandatory in order to obtain quantitative accuracy in electronic structure calculations.

Among the various models which attempt to account for triple excitations at a lower computational cost, namely $\mathcal{O}(O^3V^4)$, the most successful and economical one is the CCSD(T) approach,[22,23] where the triples contribution is added perturbatively to the CCSD energy. The CCSD(T) model has been used to calculate a variety of molecular properties[24,25] as equilibrium geometries,[26–28] dipole and quadrupole moments,[29–32] atomization energies,[33,34] vibrational frequencies,[35–39] with an accuracy comparable—and

[a)]Electronic address: coriani@univ.trieste.it

 © 2003 American Institute of Physics

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

sometimes superior—to the experimental one.

We present in this paper a novel, integral-density direct, implementation of the analytic CCSD and CCSD(T) gradients. Such approaches have been presented before in several variants for MP2,[40,41] but not for higher-order correlated methods as for instance CC models, where to our knowledge only ''conventional'' nondirect implementations have been reported.[4–13] For these methods the two-electron density is more complicated and integral-density direct implementations are more difficult to obtain. In the integral-density direct approach, both integral and density distributions in the atomic-orbital (AO) basis are calculated on the fly.

The use of canonical orbitals allows us to introduce, in a general and transparent way, the frozen-core approximation. The latter represents a fundamental approximation to reduce the number of excitations to the most relevant ones, thus contributing to extend—together with the use of an integral-density direct approach —the applicability of the CCSD(T) approach to systems with a large number of electrons. While equilibrium geometries may be determined for molecules containing first-row atoms without the use of the frozen-core approximation, the latter is more or less mandatory for molecules containing second- or higher-row elements—first, since basis sets for systematic improvement in the description of the core are often not available; second, since, even if they were, the cost of the calculation would be so high that it would prohibit the calculation to be carried out.

As a preliminary application of the new implementation, a fully analytical geometry optimization is presented for the most stable cyclic isomer of SiC_3 within the frozen-core approximation.

II. THEORY

A. The CCSD(T) energy

For a closed-shell molecule described by the Hamiltonian H, the single-reference CCSD wave function is given by the exponential *ansatz*

$$|\mathrm{CC}\rangle = \exp(T_1+T_2)|\mathrm{HF}\rangle = \exp(T)|\mathrm{HF}\rangle, \tag{1}$$

where the single and double excitation parts of the cluster operator are given by

$$T_1 = \sum_{ai} t_i^a E_{ai}, \tag{2}$$

and

$$T_2 = \frac{1}{2}\sum_{aibj} t_{ij}^{ab} E_{ai}E_{bj}, \tag{3}$$

respectively. Indices *a, b, c, d, e, f* and *i, j, k, l, m, n* refer to unoccupied and occupied molecular orbitals (MOs) in the HF reference, respectively. Indices *p, q, r, s, t, u* will be used for general MOs. In a shorthand notation the cluster operator is written as

$$T = \sum_{i=1}^{2}\sum_{\nu_i} t_{\nu_i}\tau_{\nu_i}, \tag{4}$$

where τ_{ν_i} are the excitation operators for the excitation level i, and t_{ν_i} the associated cluster amplitudes.

The CCSD energy is obtained from projection of the CC Schrödinger equation against the HF reference

$$\begin{aligned} E_{\mathrm{CCSD}} &= \langle \mathrm{HF}|\exp(-T)H\exp(T)|\mathrm{HF}\rangle \\ &= \langle \mathrm{HF}|H\exp(T)|\mathrm{HF}\rangle, \end{aligned} \tag{5}$$

and the cluster amplitudes t_{ν_i} are determined by projection against the manifold of single and double excitations out of the HF reference

$$\langle \mu_i|\exp(-T)H\exp(T)|\mathrm{HF}\rangle = 0, \quad \forall i = 1,2. \tag{6}$$

Using a biorthonormal representation[25,42] the basis of the excitation manifold $\langle \mu_i|$ is chosen such that a unit metric matrix is obtained:

$$\langle \mu_i|\tau_{\nu_j}|\mathrm{HF}\rangle = \delta_{\mu\nu}\delta_{ij}. \tag{7}$$

We assume that the HF-orbitals are determined from the canonical condition

$$F_{pq} = \delta_{pq}\epsilon_p, \tag{8}$$

where ϵ_p are the canonical orbital energies and the inactive Fock matrix elements are defined as

$$F_{pq} = \frac{1}{2}\sum_{\sigma=\alpha,\beta}\langle \mathrm{HF}|[a_{p\sigma}^{\dagger},[a_{q\sigma},H]]_+|\mathrm{HF}\rangle. \tag{9}$$

Although the canonical condition is stronger than the Brillouin condition

$$\langle \mathrm{HF}|[E_{ai}-E_{ia},H]|\mathrm{HF}\rangle = \langle \mathrm{HF}|[E_{ai}^{-},H]|\mathrm{HF}\rangle = 0, \tag{10}$$

which is equivalent to an occupied–unoccupied block diagonalization of the inactive Fock matrix, the canonical condition will be employed throughout this study since the frozen-orbital approximation is then easily accounted for.

The CCSD(T) energy is obtained from the CCSD energy by adding a perturbative correction for triple excitations

$$\begin{aligned} E_{\mathrm{CCSD(T)}} &= E_{\mathrm{CCSD}} + \sum_{\mu=\mu_1,\mu_2} t_{\mu}^{*}\langle \mu|[\Phi,T_3]|\mathrm{HF}\rangle \\ &= E_{\mathrm{CCSD}} + \sum_{\mu=\mu_1,\mu_2} t_{\mu}^{*}\langle \mu|[H,T_3]|\mathrm{HF}\rangle, \end{aligned} \tag{11}$$

where Φ is the fluctuation potential ($\Phi = H-F$). The t_{μ}^{*} are fixed linear combinations of the cluster amplitudes chosen in accordance with the biorthonormal representation

$$t_i^{*a} = 2t_i^a, \tag{12}$$

$$t_{ij}^{*ab} = 4t_{ij}^{ab} - 2t_{ji}^{ab}, \tag{13}$$

and the triple excitation amplitudes in the operator

$$T_3 = \frac{1}{6}\sum_{aibjck} t_{ijk}^{abc} E_{ai}E_{bj}E_{ck}, \tag{14}$$

are determined from the equation

$$\langle \mu_3|[F,T_3]+[H,T_2]|\mathrm{HF}\rangle = 0, \tag{15}$$

where we recall that the Fock operator is diagonal

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

$$F=\sum_{pq} F_{pq}E_{pq}=\sum_{p} \epsilon_p E_{pp}. \tag{16}$$

B. The orbital-relaxed CCSD(T) energy Lagrangian

If the molecule is subjected to an external perturbation x, the Hamiltonian becomes x-dependent $H(x)$, and the wave function responds to the perturbation. The dependence of the Hamiltonian (and of all the wave function parameters) on x is expanded in a Taylor series:

$$H(x)=H^{(0)}+H^{(1)}x+\tfrac{1}{2}H^{(2)}x^2+\cdots \tag{17}$$

The right superscript on an operator (or parameter) denotes the order of the derivative. For an arbitrary value of the external perturbation, the variational CCSD(T) energy Lagrangian allowing for orbital relaxation is constructed from Eqs. (5), (6), (8), (11), and (15) as

$$\begin{aligned} L_{\mathrm{CCSD(T)}}=&\langle \mathrm{HF}|\exp(-T)\exp(\kappa)H(x)\exp(-\kappa)\exp(T)|\mathrm{HF}\rangle+\sum_{\mu=\mu_1,\mu_2}\bar{t}_\mu\langle\mu|\exp(-T)\exp(\kappa)H(x)\\ &\times\exp(-\kappa)\exp(T)|\mathrm{HF}\rangle+\sum_{\mu=\mu_1,\mu_2}t_\mu^*\langle\mu|[\exp(\kappa)H(x)\exp(-\kappa),T_3]|\mathrm{HF}\rangle\\ &+\sum_{\mu_3}\bar{t}_{\mu_3}\langle\mu_3|\left(\left[\sum_p \epsilon_p E_{pp},T_3\right]+[\exp(\kappa)H(x)\exp(-\kappa),T_2]\right)|\mathrm{HF}\rangle+\sum_{p\geqslant q}\bar{\kappa}_{pq}(F_{pq}-\delta_{pq}\epsilon_p), \end{aligned} \tag{18}$$

where κ is the orbital-rotation operator

$$\kappa=\sum_{p\geqslant q}\kappa_{pq}E^-_{pq}. \tag{19}$$

In Eq. (18), an overbar is used to denote the Lagrange multipliers (which are multiplied by the constraint equations determining the corresponding wave-function parameters), and the *implicit* dependence of the wave-function parameters and multipliers on x has been suppressed for ease of notation. Note that the orbital energies are treated as wave function parameters, and that the t_μ^* are not independent parameters and therefore no corresponding Lagrange multipliers are needed. Note also that the corresponding CCSD[T] [formerly known as CCSD+T(CCSD)] energy Lagrangian is obtained by restricting the summation in Eq. (11) [and hence the second summation in Eq. (18)] to double excitations only. If all terms in Eq. (18) involving the triple excitation manifold (third and fourth term) are omitted, the expression for the CCSD energy Lagrangian is recovered.

For a review of the Lagrangian approach to the calculation of geometrical derivatives for nonvariational wave functions, see Refs. 1, 43.

C. The CCSD(T) molecular gradient

Following Helgaker and Jørgensen,[1,43] the first derivative with respect to the external perturbation at zero strength of the perturbation—which in case of a geometrical perturbation corresponds to the molecular gradient—can be written as

$$\begin{aligned} L^{(1)}=&\langle \mathrm{HF}|\exp(-T^{(0)})H^{(1)}\exp(T^{(0)})|\mathrm{HF}\rangle\\ &+\sum_{\mu=\mu_1,\mu_2}\bar{t}_\mu^{(0)}\langle\mu|\exp(-T^{(0)})H^{(1)}\exp(T^{(0)})|\mathrm{HF}\rangle\\ &+\sum_{\mu=\mu_1,\mu_2}t_\mu^{*(0)}\langle\mu|[H^{(1)},T_3^{(0)}]|\mathrm{HF}\rangle\\ &+\sum_{\mu_3}\bar{t}_{\mu_3}^{(0)}\langle\mu_3|[H^{(1)},T_2^{(0)}]|\mathrm{HF}\rangle+\sum_{p\geqslant q}\bar{\kappa}_{pq}^{(0)}F_{pq}^{(1)}, \end{aligned} \tag{20}$$

where full advantage has been taken of the $2n+1$ and $2n+2$ rules[1] for the wave function amplitudes and the Lagrange multipliers, respectively. Since the orbital energies are treated as wave function parameters, their derivatives are not required according to the $2n+1$ rule. In Eq. (20), $H^{(1)}$ is the first-order Hamiltonian in the orthonormalized MO (OMO) basis,[1] which consists of two contributions—the first-order Hamiltonian in the differentiated unmodified MO (UMO) basis ($H^{[1]}$) and the one-index transformed Hamiltonian representing the reorthonormalization term and containing the differentiated UMO overlap matrix $S^{[1]}$,[1]

$$H^{(1)}=H^{[1]}-\tfrac{1}{2}\{S^{[1]},H^{(0)}\}. \tag{21}$$

Here $H^{[1]}$ and $S^{[1]}$ are defined as the derivatives of H and S in the covariant AO basis, transformed to the MO basis using the undifferentiated MO coefficients. See Ref. 1 for details. The gradient may be rewritten as

$$\begin{aligned} L^{(1)}=&\sum_{pq}h_{pq}^{(1)}D_{pq}^{\mathrm{CCSD(T)}}+\frac{1}{2}\sum_{pqrs}g_{pqrs}^{(1)}d_{pqrs}^{\mathrm{CCSD(T)}}\\ &+\sum_{p\geqslant q}\bar{\kappa}_{pq}^{(0)}F_{pq}^{(1)}, \end{aligned} \tag{22}$$

in terms of CCSD(T) one- and two-electron densities

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

$$D_{pq}^{\mathrm{CCSD(T)}}=\left(\langle \mathrm{HF}|+\sum_{\mu=\mu_1,\mu_2}\bar{t}_{\mu}^{(0)}\langle\mu|\right)\times\exp(-T^{(0)})E_{pq}\exp(T^{(0)})|\mathrm{HF}\rangle+\sum_{\mu_2}t_{\mu_2}^{*(0)}\langle\mu_2|[E_{pq},T_3^{(0)}]|\mathrm{HF}\rangle\equiv D_{pq}^{\mathrm{SD}}+D_{pq}^{(\mathrm{T})},\tag{23}$$

$$d_{pqrs}^{\mathrm{CCSD(T)}}=\left(\langle \mathrm{HF}|+\sum_{\mu=\mu_1,\mu_2}\bar{t}_{\mu}^{(0)}\langle\mu|\right)\times\exp(-T^{(0)})e_{pqrs}\exp(T^{(0)})|\mathrm{HF}\rangle+\sum_{\mu=\mu_1,\mu_2}t_{\mu}^{*(0)}\langle\mu|[e_{pqrs},T_3^{(0)}]|\mathrm{HF}\rangle+\sum_{\mu_3}\bar{t}_{\mu_3}^{(0)}\langle\mu_3|[e_{pqrs},T_2^{(0)}]|\mathrm{HF}\rangle\equiv d_{pqrs}^{\mathrm{SD}}+d_{pqrs}^{(\mathrm{T})}.\tag{24}$$

Considering the re-orthonormalization terms in the derivative Hamiltonian explicitly, see Eq. (21), and recalling that the Fock matrix (to any order n) is

$$F_{pq}^{(n)}=h_{pq}^{(n)}+\sum_k(2g_{pqkk}^{(n)}-g_{pkkq}^{(n)})=h_{pq}^{(n)}+\frac{1}{2}\sum_{rs}D_{rs}^{\mathrm{HF}}(2g_{pqrs}^{(n)}-g_{prsq}^{(n)}),\tag{25}$$

where $D_{rs}^{\mathrm{HF}}=\langle\mathrm{HF}|E_{rs}|\mathrm{HF}\rangle=2\delta_{rs}\delta_{rk}$ is the HF density matrix, the gradient expression can be further simplified to

$$L^{(1)}=\sum_{pq}h_{pq}^{[1]}D_{pq}^{\mathrm{eff}}+\frac{1}{2}\sum_{pqrs}g_{pqrs}^{[1]}d_{pqrs}^{\mathrm{eff}}-\sum_{pq}S_{pq}^{[1]}F_{pq}^{\mathrm{eff}},\tag{26}$$

in terms of the variational or *effective* densities

$$D_{pq}^{\mathrm{eff}}=D_{pq}^{\mathrm{CCSD(T)}}+\bar{\kappa}_{pq}^{(0)\prime},\tag{27}$$

$$d_{pqrs}^{\mathrm{eff}}=d_{pqrs}^{\mathrm{CCSD(T)}}+2\bar{\kappa}_{pq}^{(0)\prime}D_{rs}^{\mathrm{HF}}-\bar{\kappa}_{pr}^{(0)\prime}D_{ps}^{\mathrm{HF}},\tag{28}$$

with $\bar{\kappa}_{pq}^{(0)\prime}=\frac{1}{2}(1+\delta_{pq})\bar{\kappa}_{pq}^{(0)}$ and the generalized *effective* Fock matrix

$$F_{pq}^{\mathrm{eff}}=\sum_o D_{po}^{\mathrm{eff}}h_{qo}+\sum_{ors}d_{pors}^{\mathrm{eff}}g_{qors}.\tag{29}$$

For later convenience, we also consider the gradient in the AO basis

$$L^{(1)}=\sum_{\alpha\beta}h_{\alpha\beta}^{[1]}D_{\alpha\beta}^{\mathrm{eff}}+\frac{1}{2}\sum_{\alpha\beta\gamma\delta}g_{\alpha\beta\gamma\delta}^{[1]}d_{\alpha\beta\gamma\delta}^{\mathrm{eff}}-\sum_{\alpha\beta}S_{\alpha\beta}^{[1]}F_{\alpha\beta}^{\mathrm{eff}},\tag{30}$$

with the integrals in the covariant AO basis and the densities and the effective Fock matrix transformed with the MO coefficient matrix $C_{\alpha p}$ to contravariant AO basis according to—for example,

$$D_{\alpha\beta}^{\mathrm{eff}}=\sum_{pq}(D_{pq}^{\mathrm{CCSD(T)}}+\bar{\kappa}_{pq}^{(0)\prime})C_{\alpha p}C_{\beta q}.\tag{31}$$

In Eqs. (23) and (24), the one- and two-electron densities were separated into singles and doubles terms (the first term of each equation) and into triples terms so as to highlight the similarities and differences between the densities of the CCSD(T) and CCSD models. The densities D^{SD} and d^{SD} thus collect all terms that do not explicitly contain the triple-excitation manifold. They have exactly the same structure as the densities of the CCSD method and can be calculated using the same strategy. Note, however, that, in the CCSD(T) method, the SD densities are *not* the CCSD densities, as the CCSD(T) singles and doubles multipliers are not the CCSD multipliers due to the inclusion of the triples multipliers in their right-hand side [vide infra, Eq. (43)]. The densities $D^{(\mathrm{T})}$ and $d^{(\mathrm{T})}$ represent the new contributions that must be implemented when CCSD is extended to CCSD(T).

The CCSD-like densities D^{SD} and d^{SD} are most conveniently determined in a T_1-similarity-transformed basis with the operators transformed as, for instance, $\hat{H}^{(1)}=\exp(-T_1^{(0)})H^{(1)}\exp(T_1^{(0)})$. In this basis the density D^{SD} simplifies to

$$D_{\alpha\beta}^{\mathrm{SD}}=\sum_{pq}\tilde{D}_{pq}^{\mathrm{SD}}\Lambda_{\alpha p}^{p}\Lambda_{\beta q}^{h},\tag{32}$$

$$\tilde{D}_{pq}^{\mathrm{SD}}=\left(\langle\mathrm{HF}|+\sum_{\mu=\mu_1,\mu_2}\bar{t}_{\mu}^{(0)}\langle\mu|\right)\times\exp(-T_2^{(0)})E_{pq}\exp(T_2^{(0)})|\mathrm{HF}\rangle,\tag{33}$$

and similar equations hold for the two-electron part. Note that $\tilde{D}^{\mathrm{SD}}$ no longer contains the singles amplitudes. The integrals of the T_1-transformed operators are conversely obtained as for instance

$$\hat{h}_{pq}=\sum_{rs}h_{rs}(\mathbf{1}-\mathbf{t}_1)_{pr}(\mathbf{1}+\mathbf{t}_1)_{sq}\equiv\sum_{\alpha\beta}h_{\alpha\beta}\Lambda_{\alpha p}^{p}\Lambda_{\beta r}^{h},\tag{34}$$

where Λ^p and Λ^h are modified MO coefficient matrices for the similarity transformed basis[15,16,44]

$$\mathbf{\Lambda}^p=\mathbf{C}(\mathbf{1}-\mathbf{t}_1^T)\tag{35}$$

$$\mathbf{\Lambda}^h=\mathbf{C}(\mathbf{1}+\mathbf{t_1}),\tag{36}$$

with

$$\mathbf{t}_1=\begin{pmatrix}\mathbf{0} & \mathbf{0}\\ \{t_i^a\} & \mathbf{0}\end{pmatrix}.\tag{37}$$

If necessary, the one-electron density in the regular MO basis can be obtained from the density in the T_1-transformed basis via the transformation

$$D_{pq}^{\mathrm{SD}}=\sum_{rs}\tilde{D}_{rs}^{\mathrm{SD}}(\mathbf{1}-\mathbf{t}_1)_{rp}(\mathbf{1}+\mathbf{t}_1^T)_{sq}.\tag{38}$$

A similar expression holds for the partially backtransformed two-electron density $d_{pq\gamma\delta}^{\mathrm{SD}}$.

D. CCSD(T) first-order one-electron properties

Expressions for first-order one-electron properties, like the molecular electric dipole moment, are conveniently obtained from the expression for the full gradient by omitting

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

the two-electron part and all the reorthonormalization terms in the Hamiltonian derivative, keeping only $h^{[1]}$ as perturbation:

$$\langle h^{[1]}\rangle = \langle \mathrm{HF}|\exp(-T^{(0)})h^{[1]}\exp(T^{(0)})|\mathrm{HF}\rangle + \sum_{\mu_2} t^{*(0)}_{\mu_2}\langle \mu_2|[h^{[1]},T_3^{(0)}]|\mathrm{HF}\rangle + \sum_{\mu=\mu_1,\mu_2}\overline{t}^{(0)}_{\mu}\langle \mu|\exp(-T^{(0)})h^{[1]}\exp(T^{(0)})|\mathrm{HF}\rangle + \sum_{p\geqslant q}\overline{\kappa}^{(0)}_{pq}h^{[1]}_{pq}. \quad (39)$$

This expression, as the one in Eq. (23), has been simplified compared to Eq. (20) from a consideration of excitation levels and operator ranks. It is conveniently rewritten in terms of the effective one-electron density matrix as

$$\langle h^{[1]}\rangle = \sum_{pq} h^{[1]}_{pq}D^{\mathrm{eff}}_{pq}. \quad (40)$$

The orbital-relaxed first-order one-electron properties are thus determined from the contraction of the effective one electron density D^{eff}_{pq} with the property integrals $h^{[1]}_{pq}$.

E. The CCSD(T) response equations

The zero-order cluster amplitudes are determined from Eqs. (6) and (15), while the equations for the zero-order multipliers are obtained by requiring the Lagrangian to be stationary with respect to the cluster amplitudes. The triples amplitude multipliers are determined by the condition $\partial L^{(0)}/\partial t^{(0)}_{\nu_3}=0$:

$$0 = \sum_{\mu=\mu_1,\mu_2} t^{*(0)}_{\mu}\langle \mu|[H^{(0)},\tau_{\nu_3}]|\mathrm{HF}\rangle + \sum_{\mu_3}\overline{t}^{(0)}_{\mu_3}\langle \mu_3|[F^{(0)},\tau_{\nu_3}]|\mathrm{HF}\rangle \quad (41)$$

$$\Leftrightarrow$$

$$\overline{t}^{(0)}_{\nu_3} = -\frac{1}{\epsilon^{(0)}_{\nu_3}}\sum_{\mu=\mu_1,\mu_2} t^{*(0)}_{\mu}\langle \mu|[H^{(0)},\tau_{\nu_3}]|\mathrm{HF}\rangle, \quad (42)$$

where $\epsilon^{(0)}_{\nu_3}$ is the sum of HF orbital energy differences for the triple substitution ν_3. For the single and double amplitude multipliers, we obtain the equations

$$\frac{\partial L^{(0)}}{\partial t^{(0)}_{\nu}}=0,\ \forall\,\nu=\nu_1,\nu_2 \Leftrightarrow$$

$$0 = \sum_{\mu=\mu_1,\mu_2}\overline{t}^{(0)}_{\mu}\langle \mu|\exp(-T^{(0)})[H^{(0)},\tau_{\nu}]\exp(T^{(0)})|\mathrm{HF}\rangle + \langle \mathrm{HF}|\exp(-T^{(0)})[H^{(0)},\tau_{\nu}]\exp(T^{(0)})|\mathrm{HF}\rangle + \langle \nu^*|[H^{(0)},T_3^{(0)}]|\mathrm{HF}\rangle + \sum_{\mu_3}\overline{t}^{(0)}_{\mu_3}\langle \mu_3|[H^{(0)},\tau_{\nu}]|\mathrm{HF}\rangle, \quad \forall\,\nu=\nu_1,\nu_2, \quad (43)$$

where $\langle \nu^*|$ is the same linear combination of excited configurations as the linear combination of amplitudes in $t^{*(0)}$ [Eqs. (12) and (13)]—that is, $\langle {}^{a}_{i}*|=2\langle {}^{a}_{i}|$ and $\langle {}^{ab}_{ij}*|=4\langle {}^{ab}_{ij}|-2\langle {}^{ab}_{ji}|$—and the last term in Eq. (43) only contributes for ν_2. Finally,

$$\frac{\partial L^{(0)}}{\partial \epsilon^{(0)}_{p}}=0 \Leftrightarrow$$

$$\overline{\kappa}^{(0)}_{pp} = \sum_{\mu_3}\overline{t}^{(0)}_{\mu_3}\langle \mu_3|[E_{pp},T_3^{(0)}]|\mathrm{HF}\rangle, \quad (44)$$

determines the diagonal part of the orbital-rotation multiplier matrix, and

$$\frac{\partial L^{(0)}}{\partial \kappa^{(0)}_{rs}}=0, \quad \forall r>s \Leftrightarrow$$

$$0 = \sum_{p\geqslant q}\overline{\kappa}^{(0)}_{pq}\frac{1}{2}\sum_{\sigma}\langle \mathrm{HF}|[a^{\dagger}_{p\sigma},[a_{q\sigma},[E^{-}_{rs},H^{(0)}]]]_{+}|\mathrm{HF}\rangle + \langle \mathrm{HF}|\exp(-T^{(0)})[E^{-}_{rs},H^{(0)}]\exp(T^{(0)})|\mathrm{HF}\rangle + \sum_{\mu=\mu_1,\mu_2} t^{*(0)}_{\mu}\langle \mu|[[E^{-}_{rs},H^{(0)}],T_3^{(0)}]|\mathrm{HF}\rangle + \sum_{\mu=\mu_1,\mu_2}\overline{t}^{(0)}_{\mu}\langle \mu|\exp(-T^{(0)})[E^{-}_{rs},H^{(0)}]\exp(T^{(0)})|\mathrm{HF}\rangle + \sum_{\mu_3}\overline{t}^{(0)}_{\mu_3}\langle \mu_3|[[E^{-}_{rs},H^{(0)}],T_2^{(0)}]|\mathrm{HF}\rangle, \quad \forall r>s, \quad (45)$$

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

gives the off-diagonal part. Note that the diagonal orbital-rotation multipliers are trivially zero in the CCSD case. Equation (45) is the coupled-perturbed HF (CPHF) equation, also known as the *Z*-vector equation

$$\overline{\boldsymbol{\kappa}}^{(0)}\mathbf{A}=\overline{{}^{\kappa}\boldsymbol{\eta}}, \tag{46}$$

with the right-hand side

$$\begin{aligned}\overline{{}^{\kappa}\eta}_{pq}^{\mathrm{CCSD(T)}}=&\left(\langle \mathrm{HF}|+\sum_{\mu=\mu_1,\mu_2}\overline{t}_{\mu}^{(0)}\langle\mu|\right)\exp(-T^{(0)})\\&\times[H^{(0)},E_{rs}^{-}]\exp(T^{(0)})|\mathrm{HF}\rangle\\&+\sum_{\mu=\mu_1,\mu_2}t_{\mu}^{*(0)}\langle\mu|[[H^{(0)},E_{pq}^{-}],T_3^{(0)}]|\mathrm{HF}\rangle\\&+\sum_{\mu_3}\overline{t}_{\mu_3}^{(0)}\langle\mu_3|[[H^{(0)},E_{pq}^{-}],T_2^{(0)}]|\mathrm{HF}\rangle\\\equiv&\,\overline{{}^{\kappa}\eta}_{pq}^{\mathrm{SD}}+\overline{{}^{\kappa}\eta}_{pq}^{(\mathrm{T})}.\end{aligned} \tag{47}$$

Expressions for the matrix **A** can be found, for instance, in Ref. 45. In Eq. (47), the vector $\overline{{}^{\kappa}\eta}_{pq}^{\mathrm{CCSD(T)}}$ is written as a sum of SD and (T) contributions, where the SD part—the first term in Eq. (47)—is structurally identical to the CCSD right-hand side. After some manipulation and using the commutation relationships

$$[h,E_{pq}]=\sum_{r}(h_{rp}E_{rp}-h_{qr}E_{pr}), \tag{48}$$

$$\frac{1}{2}[g,E_{pq}]=\sum_{rst}(g_{rstp}e_{stp}-g_{rsqt}e_{ptrs}), \tag{49}$$

where *h* and *g* on the left-hand side are one- and two-electron parts of the (undifferentiated) Hamiltonian in second quantization, the right-hand side can be rewritten in terms of the previously defined densities and the undifferentiated integrals

$$\begin{aligned}\overline{{}^{\kappa}\eta}_{pq}^{\mathrm{CCSD(T)}}=(1-P_{pq})\Bigg\{&\sum_{t}(D_{tq}^{\mathrm{CCSD(T)}}+D_{qt}^{\mathrm{CCSD(T)}})h_{pt}\\&+\sum_{trs}(d_{tqrs}^{\mathrm{CCSD(T)}}+d_{qtrs}^{\mathrm{CCSD(T)}})g_{ptrs}\Bigg\}.\end{aligned} \tag{50}$$

The density form of the CCSD-like and (T) contributions is immediately identified by inserting the decomposition of the densities, Eqs. (23) and (24). The present density-based implementation of the right-hand side of the orbital-rotation multiplier equations is described in Sec. III D.

III. IMPLEMENTATION

The CCSD(T) gradient and first-order-properties have been implemented (with the corresponding CCSD properties as special cases)[47] in the DALTON code.[46] Furthermore the MP2 and CC2 gradient and first-order-properties have also been implemented.

A crucial step in the calculation of first-order properties and gradients of correlated methods is the construction of the two-electron density matrix and its contraction with (1) undifferentiated integrals to the inhomogenity of the *Z*-vector equations $\overline{{}^{\kappa}\eta}$ and the effective Fock matrix F^{eff} and (2) the differentiated integrals to the two-electron contribution to the gradient. To avoid N^4 storage bottlenecks which would hinder any large-scale applications, neither the density nor the integrals should be stored as a complete set on disk. Both the density and the integrals must be calculated on the fly and contracted in a direct manner to obtain the final results. Such algorithms have been used before in integral-direct and semi-direct implementations of MP2 gradients,[40,41] but to our knowledge no integral-density direct implementation of CC gradients has yet been reported. To implement an integral-density direct algorithm, the two-electron density must be constructed with one or two fixed indices (or index shells) in the AO basis, making its construction even more complex. For the present implementation, we have chosen a strategy with one fixed index in the AO basis, which is most conveniently combined with the integral-direct CCSD approach described in Refs. 15, 16. Our strategy can be outlined as follows:

- precalculate some intermediates which can be stored in memory or on disk
- loop over Δ (where Δ is a subset of basis functions belonging to the same shell and related by symmetry)
  - —depending on what the requested result is
    - calculate $d_{pq\gamma\delta}\,\forall p,q,\gamma$ or $d_{\alpha\beta\gamma\delta}\,\forall\alpha,\beta,\gamma$ and $\forall\,\delta\in\Delta$
    - calculate $g_{\alpha\beta\gamma\delta}\,\forall\,\alpha,\beta,\gamma$ and $\forall\,\delta\in\Delta$ and contract with $d_{\alpha\beta\gamma\delta}$ to the corresponding contribution to F^{eff}, or calculate $g_{pq\gamma\delta}\forall p,q,\gamma$ and contract with $d_{pq\gamma\delta}\forall p,q,\gamma$ to the corresponding contribution to ${}^{\kappa}\eta$
    - calculate $g^{[x]}_{\alpha\beta\gamma\delta}$ and contract with $d_{\alpha\beta\gamma\delta}$ to the two-electron contribution to the gradient
- end loop Δ

We thus avoid storage of $\mathcal{O}(N^4)$ intermediates on disk and can keep the memory requirements as low as for the solution of the cluster equations. Considerations about the implementation of the CCSD gradient along these lines are also given in Ref. 47, and the calculation of CCSD first-order properties within such a scheme has been described in Ref. 14. In the following, we describe the implementation of this strategy for the two-electron density, the intermediates $\overline{{}^{\kappa}\eta}$ and F^{eff}, and the two-electron contribution to the gradient in some detail, with special emphasis on the contributions from the triple substitutions needed for CCSD(T) first-order properties and gradients.

A. The response equations

The Lagrange multipliers $\overline{t}_{\nu_3}$ for the triples amplitudes are determined by Eq. (42). The two contributions to the right-hand side become

$$\sum_{ai}t_i^{*a}\langle_i^a|[H^{(0)},\tau_{lmn}^{def}]|\mathrm{HF}\rangle=P_{lmn}^{def}(L_{menf}t_l^{*d}-L_{melf}t_n^{*d}), \tag{51}$$

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

$$\sum_{aibj} t_{ij}^{*ab}\langle_{ij}^{ab}|[H^{(0)},\tau_{lmn}^{def}]|\mathrm{HF}\rangle$$

$$= P_{lmn}^{def}\Big[t_{lm}^{*de}F_{nf} - t_{ln}^{*de}F_{mf} - \sum_i t_{li}^{*de}L_{minf} + \sum_i t_{in}^{*de}g_{limf} + \sum_a t_{lm}^{*da}L_{aenf} - \sum_a t_{mn}^{*da}g_{leaf}\Big], \quad (52)$$

with $L_{pqrs}=2g_{pqrs}-g_{psrq}$. Inserting the above expressions in Eq. (42) gives the following expression for the triples multipliers:

$$\overline{t}_{lmn}^{def} = -\frac{1}{\epsilon_{lmn}^{def}} P_{lmn}^{def}\Big(L_{menf}t_l^{*d} - L_{melf}t_n^{*d} + t_{lm}^{*de}F_{nf} - t_{ln}^{*de}F_{mf} - \sum_i t_{li}^{*de}L_{minf} + \sum_i t_{in}^{*de}g_{limf} + \sum_a t_{lm}^{*da}L_{aenf} - \sum_h t_{mn}^{*da}g_{leaf}\Big), \quad (53)$$

where $\epsilon_{lmn}^{def}=\epsilon_d-\epsilon_l+\epsilon_e-\epsilon_m+\epsilon_f-\epsilon_n$ and the symmetrization operator P_{ijk}^{abc} is defined as

$$P_{ijk}^{abc}(A_{ijk}^{abc}) = A_{ijk}^{abc}+A_{ikj}^{acb}+A_{jik}^{bac}+A_{kji}^{cba}+A_{kij}^{cab}+A_{jki}^{bca}. \quad (54)$$

Note that we often omit the superscript (0) in the amplitudes, multipliers and integrals for ease of notation.

For the singles and doubles multipliers, we need to solve Eq. (43). The first two terms are structurally identical to the CCSD terms, and their integral-direct implementation is described in detail elsewhere.[14] Only the triples specific terms in the equation are considered here. These are found as

$$\langle_i^a *|[H^{(0)},T_3^{(0)}]|\mathrm{HF}\rangle = 2\sum_{ckdl}(t_{ikl}^{acd}-t_{kil}^{acd})L_{ldkc}, \quad (55)$$

$$\langle_{ij}^{ab}|_{ij}^{ad} *|[H^{(0)},T_3^{(0)}]|\mathrm{HF}\rangle = P_{aibj}^{\mathrm{TCME}}\Big\{ 2P_{ij}^{ab}\Big[\sum_{ck}(t_{ijk}^{abc}-t_{ikj}^{abc})F_{kc} - \sum_{ckl}(2t_{ilk}^{abc}-t_{kli}^{abc} - t_{ikl}^{abc})g_{ljkc} + \sum_{ckd}(2t_{ikj}^{acd}-t_{kij}^{acd}-t_{ijk}^{acd})g_{bdkc}\Big]\Big\}, \quad (56)$$

and

$$\sum_{\mu_3}\overline{t}_{\mu_3}^{(0)}\langle\mu_3|[H^{(0)},\tau_{ij}^{ab}]|\mathrm{HF}\rangle = P_{ij}^{ab}\Big(\sum_{ckd}\overline{t}_{ikj}^{acd}g_{ckdb} - \sum_{ckl}\overline{t}_{ikl}^{acb}g_{ckjl}\Big), \quad (57)$$

with the symmetrization operators

$$P_{ij}^{ab}A_{ij}^{ab} = A_{ij}^{ab}+A_{ji}^{ba}, \quad (58)$$

$$P_{aibj}^{\mathrm{TCME}}A_{ij}^{ab} = 2A_{ij}^{ab}-A_{ji}^{ab}. \quad (59)$$

Note that the contributions in Eqs. (55) and (56) are similar to two triples specific terms in the ground-state amplitude equations for the CC3 model—see terms (IX) and (X) in Table I of Ref. 48—differing only, in Eq. (56), by the operator P_{aibj}^{TCME} defined in Eq. (59) and in that the integrals refer to the usual MO basis instead of the T_1-transformed basis. The implementation is thus basically identical to the implementation presented for the CC3 ground-state energy in Ref. 48, just with slightly different integrals and followed by the application of the P_{aibj}^{TCME} operator on the doubles result vector. The contributions from the triples multipliers explicitly given in Eq. (57) are quite similar to the last two contributions in Eq. (56), with the triples multipliers in place of the triples amplitudes. Since the multipliers $\overline{t}_{\nu_3}$ have a structure similar to that of the zero-order triples cluster amplitudes—that is, they can be written in the form

$$X_{ijk}^{abc} = -\frac{1}{\epsilon_{ijk}^{abc}}P_{ijk}^{abc}(\tilde{X}_{ijk}^{abc}), \quad (60)$$

where $\tilde{X}_{ijk}^{abc}$ is one of the six permutational components in Eq. (53), we may implement the terms in Eq. (57) via S and Q intermediates similar to those introduced in the calculation of the contribution from the triples amplitudes to the CC3 ground state vector function described in Ref. 48. For the triples Lagrange multipliers, the S and Q matrices can be identified from Eqs. (53) and (60), recalling that the general definitions are:[48]

$$S^{bc}(aikj) = -\frac{1}{\epsilon_{ijk}^{abc}}(\tilde{X}_{ijk}^{abc}+\tilde{X}_{jik}^{bac}), \quad (61)$$

$$Q^{bc}(aijk) = -\frac{1}{\epsilon_{ijk}^{abc}}\tilde{X}_{ikj}^{acb}. \quad (62)$$

TABLE I. The one-electron SD and (T) densities. Note that the SD density is in the Λ^p, Λ^h-basis, whereas the (T) density is in the regular MO basis.

Correlated space
$\tilde{D}_{ai}^{\mathrm{SD}}=\overline{t}_i^a$
$\tilde{D}_{ab}^{\mathrm{SD}}=\Sigma_{ckl}t_{kl}^{cb}\overline{t}_{kl}^{ca}\equiv Y_{ba}$
$\tilde{D}_{ij}^{\mathrm{SD}}=2\delta_{ij}-\Sigma_{cdk}t_{ki}^{cd}\overline{t}_{kj}^{cd}\equiv 2\delta_{ij}-X_{ij}$
$\tilde{D}_{ia}^{\mathrm{SD}}=\Sigma_{bj}\overline{t}_j^b(2t_{ij}^{ab}-t_{ij}^{ba})\equiv\Sigma_{bj}\overline{t}_j^b\tilde{t}_{ij}^{ab}\equiv\varepsilon_{ai}$
...
$D_{ia}^{(\mathrm{T})}=2\Sigma_{dlem}(t_{lmi}^{dea}-t_{lim}^{dea})t_{lm}^{*de}$
Additional frozen-core term
$D_{IJ}^{\mathrm{SD}}=2\delta_{IJ}$

B. The one-electron densities

Explicit expressions for the one-electron density $\tilde{D}^{\mathrm{SD}}$ in the T_1-transformed basis, which are easily found from the equation

$$\tilde{D}_{pq}^{\mathrm{SD}} = \Big(\langle\mathrm{HF}| + \sum_{\mu=\mu_1,\mu_2}\overline{t}_\mu\langle\mu|\Big)\{E_{pq}+[E_{pq},T_2]\}|\mathrm{HF}\rangle, \quad (63)$$

are collected in Table I. The implementation of $\tilde{D}^{\mathrm{SD}}$ does not present any complication and will not be discussed further here. The triples contribution to the one-electron density is found from

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

TABLE II. The symmetry-unique blocks of the CCSD-like two-electron density in the Λ^p, Λ^h-basis. The intermediates are $\tilde{t}^{cd}_{kl}=2t^{cd}_{kl}-t^{cd}_{lk}$; $\varepsilon_{ck}=\Sigma_{dl}\tilde{t}^{cd}_{kl}\overline{t}^{d}_{l}$; $\tilde{M}_{ijm,n}=\Sigma_{cd}\overline{t}^{cd}_{jn}t^{cd}_{im}$; $X_{ij}=\Sigma_{cdk}t^{cd}_{ki}\overline{t}^{cd}_{kj}$; $Y_{ab}=\Sigma_{ckl}t^{ca}_{kl}\overline{t}^{cb}_{kl}$.

Correlated space

$$\tilde{d}^{\mathrm{SD}}_{ijkl}=4\delta_{ij}\delta_{kl}-2\delta_{kj}\delta_{il}+\delta_{kj}\Sigma_{cdm}\overline{t}^{cd}_{ml}t^{cd}_{mi}-2\delta_{ij}\Sigma_{cdm}\overline{t}^{cd}_{ml}t^{cd}_{mk}$$
$$-2\delta_{kl}\Sigma_{cdm}\overline{t}^{cd}_{mj}t^{cd}_{mi}+\delta_{il}\Sigma_{cdm}\overline{t}^{cd}_{mj}t^{cd}_{mk}+\Sigma_{cd}\overline{t}^{cd}_{jl}t^{cd}_{ik}$$
$$\equiv 4\delta_{ij}\delta_{kl}-2\delta_{kj}\delta_{il}+\delta_{kj}X_{il}-2\delta_{ij}X_{kl}-2\delta_{kl}X_{ij}+\delta_{il}X_{kj}+\tilde{M}_{ijkl}$$
$$\tilde{d}^{\mathrm{SD}}_{ijka}=2\delta_{ij}\Sigma_{cl}\overline{t}^{c}_{l}\tilde{t}^{ac}_{kl}-\delta_{jk}\Sigma_{cl}\overline{t}^{c}_{l}\tilde{t}^{ac}_{il}-\Sigma_{c}\overline{t}^{c}_{j}\tilde{t}^{ac}_{ki}$$
$$\equiv 2\delta_{ij}\varepsilon_{ak}-\delta_{jk}\varepsilon_{ai}-\Sigma_{c}\overline{t}^{c}_{j}\tilde{t}^{ac}_{ki}$$
$$\tilde{d}^{\mathrm{SD}}_{ijab}=2\delta_{ij}\Sigma_{ckl}\overline{t}^{ca}_{kl}t^{cb}_{kl}-\Sigma_{ck}\overline{t}^{ca}_{kj}t^{cb}_{ki}-\Sigma_{ck}\overline{t}^{ca}_{jk}t^{cb}_{ik}$$
$$\equiv 2\delta_{ij}Y_{ba}-\Sigma_{ck}\overline{t}^{ca}_{kj}t^{cb}_{ki}-\Sigma_{ck}\overline{t}^{ca}_{jk}t^{cb}_{ik}$$
$$\tilde{d}^{\mathrm{SD}}_{iajb}=2\tilde{t}^{ab}_{ij}+\Sigma_{ckem}\overline{t}^{ea}_{mi}t^{ec}_{mk}\tilde{t}^{cb}_{kj}+\Sigma_{ckem}t^{ab}_{mk}t^{ce}_{ij}\overline{t}^{ce}_{mk}-\Sigma_{ckem}\tilde{t}^{eb}_{ij}t^{ca}_{km}\overline{t}^{ce}_{km}$$
$$-\Sigma_{ckem}\tilde{t}^{ab}_{mj}t^{ce}_{ki}\overline{t}^{ce}_{km}-\Sigma_{ckem}\tilde{t}^{ab}_{im}t^{ce}_{kj}\overline{t}^{ce}_{km}-\Sigma_{ckem}\tilde{t}^{ac}_{ij}t^{eb}_{km}\overline{t}^{ec}_{km}$$
$$-\Sigma_{ckem}t^{ca}_{kj}\tilde{t}^{eb}_{mi}\overline{t}^{ce}_{km}+\Sigma_{ckem}t^{ac}_{kj}t^{eb}_{mi}\overline{t}^{ce}_{km}+\Sigma_{ckem}t^{ac}_{kj}t^{eb}_{im}\overline{t}^{ce}_{mk}$$
$$\equiv 2\tilde{t}^{ab}_{ij}+\Sigma_{ckem}\tilde{t}^{cb}_{kj}\tilde{t}^{ea}_{mi}\overline{t}^{ec}_{mk}+\Sigma_{km}t^{ab}_{mk}\tilde{M}_{imjk}-\Sigma_{e}\tilde{t}^{eb}_{ij}Y_{ae}-\Sigma_{m}\tilde{t}^{ab}_{mj}X_{im}$$
$$-\Sigma_{m}\tilde{t}^{ab}_{im}X_{jm}-\Sigma_{c}\tilde{t}^{ac}_{ij}Y_{bc}-\Sigma_{ckem}t^{ca}_{kj}\tilde{t}^{eb}_{mi}\overline{t}^{ce}_{mk}$$
$$+\Sigma_{ckem}t^{ac}_{kj}t^{eb}_{mi}\overline{t}^{ce}_{km}+\Sigma_{ckem}t^{ac}_{kj}t^{eb}_{im}\overline{t}^{ce}_{mk}$$
$$\tilde{d}^{\mathrm{SD}}_{aibj}=\overline{t}^{ab}_{ij}$$
$$\tilde{d}^{\mathrm{SD}}_{aijk}=2\delta_{jk}\overline{t}^{a}_{i}-\delta_{ij}\overline{t}^{a}_{k}$$
$$\tilde{d}^{\mathrm{SD}}_{aijb}=\Sigma_{dk}\overline{t}^{ad}_{ik}\tilde{t}^{db}_{kj}-\delta_{ij}\Sigma_{ckl}\overline{t}^{ca}_{kl}t^{cb}_{kl}\equiv\Sigma_{dk}\overline{t}^{ad}_{ik}\tilde{t}^{db}_{kj}-\delta_{ij}Y_{ba}$$
$$\tilde{d}^{\mathrm{SD}}_{abic}=\Sigma_{m}\overline{t}^{a}_{m}\tilde{t}^{bc}_{mi}$$
$$\tilde{d}^{\mathrm{SD}}_{abcd}=\Sigma_{mn}\overline{t}^{ac}_{mn}t^{bd}_{mn}$$

Additional frozen-core terms

$$\tilde{d}^{\mathrm{SD}}_{IJKL}=4\delta_{IJ}\delta_{KL}-2\delta_{KJ}\delta_{IL}$$
$$\tilde{d}^{\mathrm{SD}}_{ijKL}=4\delta_{ij}\delta_{KL}-2\delta_{KL}\Sigma_{cdm}\overline{t}^{cd}_{mj}t^{cd}_{mi}\equiv 4\delta_{ij}\delta_{KL}-2\delta_{KL}X_{ij}$$
$$\tilde{d}^{\mathrm{SD}}_{iJKl}=-2\delta_{KJ}\delta_{il}+\delta_{KJ}\Sigma_{cdm}\overline{t}^{cd}_{ml}t^{cd}_{mi}\equiv-2\delta_{KJ}\delta_{il}+\delta_{KJ}X_{il}$$
$$\tilde{d}^{\mathrm{SD}}_{IJka}=2\delta_{IJ}\Sigma_{cl}\overline{t}_{cl}\tilde{t}_{ak,cl}\equiv 2\delta_{IJ}\varepsilon_{ak}$$
$$\tilde{d}^{\mathrm{SD}}_{iJKa}=-\delta_{JK}\Sigma_{cl}\overline{t}_{cl}\tilde{t}_{ai,cl}\equiv-\delta_{JK}\varepsilon_{ai}$$
$$\tilde{d}^{\mathrm{SD}}_{aIJk}=-\delta_{IJ}\overline{t}^{a}_{k}$$
$$\tilde{d}^{\mathrm{SD}}_{aiJK}=2\delta_{JK}\overline{t}^{a}_{i}$$
$$\tilde{d}^{\mathrm{SD}}_{IJab}=2\delta_{IJ}\Sigma_{ckl}\overline{t}^{ca}_{kl}t^{cb}_{kl}\equiv 2\delta_{IJ}Y_{ba}$$
$$\tilde{d}^{\mathrm{SD}}_{aIJb}=-\delta_{IJ}\Sigma_{ckl}\overline{t}^{ca}_{kl}t^{cb}_{kl}\equiv-\delta_{IJ}Y_{ba}$$

$$D^{(\mathrm{T})}_{pq}=\sum_{aibj}t^{*ab}_{ij}\langle{}^{ab}_{ij}|[E_{pq},T_3]|\mathrm{HF}\rangle. \tag{64}$$

Within the canonical formulation, the only nonvanishing contribution appears in the occupied-virtual block:

$$D^{(\mathrm{T})}_{ia}=2\sum_{dlem}(t^{dea}_{lmi}-t^{dea}_{lim})t^{*de}_{lm}. \tag{65}$$

It is very similar in structure to Eq. (55) and to the triples contribution to the single excitation part of the CC3 vector function, with t^{*ab}_{ij} replacing an L_{iajb} integral. Therefore, the implementation of the density block in Eq. (65) follows the implementation of that particular contribution, see Ref. 48. The density $D^{(\mathrm{T})}$ is precalculated and stored on disk for later use in the calculation of the inhomogenity for the Z-vector equation ${}^{\kappa}\eta^{\mathrm{CCSD(T)}}$ Eq. (47) and for the gradient.

C. The two-electron densities and the integral-density direct algorithm

The CCSD-like two-electron density $\tilde{d}^{\mathrm{SD}}$ in the T_1-transformed basis is obtained as

$$\tilde{d}^{\mathrm{SD}}_{pqrs}=\langle\mathrm{HF}|e_{pqrs}+[e_{pqrs},T_2]|\mathrm{HF}\rangle$$
$$+\sum_{\mu=\mu_1,\mu_2}\overline{t}_{\mu}\langle\mu|\Big\{e_{pqrs}+[e_{pqrs},T_2]$$
$$+\frac{1}{2}[[e_{pqrs},T_2],T_2]\Big\}|\mathrm{HF}\rangle. \tag{66}$$

The explicit expressions for the various blocks of the SD two-electron density in the T_1-transformed MO basis are given in Table II. We shall return to the implementation of the CCSD-like two-electron density later in this section.

The symmetry-unique blocks of the triples contribution to the two-electron density $d^{(\mathrm{T})}$ are presented later (see Table IV). These contributions cannot be evaluated efficiently from the amplitudes and the Lagrange multipliers on the fly, with one index in the AO basis. Therefore, they are precalculated in the MO basis as described below and stored on disk. This is possible since these densities require at most $\mathcal{O}(OV^3)$ disk space (vide infra), which does not constitute a serious bottleneck in CCSD(T) calculations.

The density $d^{(\mathrm{T})}_{iajb}$ is similar to the Fock contribution to the double excitation part of the vector function in a CC3 ground-state energy calculation [cf. Fock contribution in Eq. (56)] and is therefore implemented the same way, with t^{*d}_{l} replacing the Fock matrix element.[48]

The first term in $d^{(\mathrm{T})}_{iajk}$ and the only term in $d^{(\mathrm{T})}_{aijk}$ are similar and calculated in the same manner—for example,

$$d^{(\mathrm{T})}_{aijk}=-\sum_{dle}\overline{t}^{dea}_{lki}t^{de}_{lj}$$
$$=-\sum_{dle}\{S^{ae}(dlki)+Q^{ae}(dlik)$$
$$+S^{ad}(ekli)+Q^{ad}(ekil)\}t^{de}_{lj}$$
$$=-\sum_{dle}\{[S^{ae}(dlki)+Q^{ae}(dlik)]t^{de}_{lj}$$
$$+[S^{ae}(dkli)+Q^{ae}(dkil)]t^{ed}_{lj}\}. \tag{67}$$

The second and third term in $d^{(\mathrm{T})}_{iajk}$ can be seen to be equal to the density $D^{(\mathrm{T})}_{ia}$ in Eq. (65) multiplied by a Kronecker delta and are easily evaluated.

The most difficult blocks to calculate are the densities $d^{(\mathrm{T})}_{abci}$ and $d^{(\mathrm{T})}_{abjc}$. They cannot be stored in memory due to their size OV^3 as we allow at most objects of size O^2V^2 in memory. The two densities are very similar and so is their implementation—for example,

$$d^{(\mathrm{T})}_{abci}=-\sum_{dlm}\overline{t}^{dac}_{lmi}t^{db}_{lm}$$
$$=-\sum_{dle}\{[S^{dc}(amil)+Q^{dc}(amli)]t^{db}_{lm}$$
$$+[S^{da}(ciml)+Q^{da}(cilm)]t^{db}_{lm}\}. \tag{68}$$

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

To obtain $d^{(\mathrm{T})}_{abci}$, we store two different intermediate densities on disk. One is stored with a as the outer index and the other with c as the outer index. Next, the two intermediates are added together.

To prepare the density $d^{(\mathrm{T})}$ for contraction with two-electron AO integrals, the last index of each block is back-transformed to the contravariant AO basis and the density is stored as $d^{(\mathrm{T})}_{pqr\delta}$ on disk. More specifically, taking advantage of the full permutational symmetry of the MO integrals, the (T) density blocks $d^{(\mathrm{T})}_{abci}$ and $d^{(\mathrm{T})}_{abic}$ are added together to give the symmetrized density ${}^{S}d^{(\mathrm{T})}_{abic}$, which is then backtransformed to ${}^{S}d^{(\mathrm{T})}_{abi\delta}$. A similar strategy is used with the $d^{(\mathrm{T})}_{ijka}$ and $d^{(\mathrm{T})}_{ijak}$ blocks to obtain ${}^{S}d^{(\mathrm{T})}_{ijk\delta}$. This gives maximum I/O and storage requirements of the order V^2NO.

As pointed out at the beginning of Sec. III, an integral-density direct implementation of first derivatives requires that the two-electron density can be calculated efficiently in a loop over basis functions with at least one index transformed to the AO basis. The CCSD-like contributions $\tilde{d}^{\mathrm{SD}}$ cannot be precalculated in the MO basis and stored on disk as done for the triples contribution $d^{(\mathrm{T})}$. Thus these density contributions must be formulated with one back-transformed index to allow for an on-the-fly construction of $d^{\delta}_{pq,r}$ in a loop over δ from some smaller intermediates. (Note that we allow, as in the implementation of the CCSD vector function,[15,16] at most intermediates of the size O^2V^2 in memory.) Such a reformulation is presented in Table III. Assuming that the triples contributions ${}^{S}d^{(\mathrm{T})}_{abi\delta}$, ${}^{S}d^{(\mathrm{T})}_{ijk\delta}$, $d^{(\mathrm{T})}_{aij\delta}$, $d^{(\mathrm{T})}_{aib\delta}$, $d^{(\mathrm{T})}_{iaj\delta}$, $d^{(\mathrm{T})}_{iab\delta}$ are already available on disk, the algorithm for the calculation of d^{δ}_{pqr} can be sketched as follows:

- precalculate the intermediates X_{ij}, Y_{ab}, $\tilde{M}_{ijm,n}$, $\varepsilon_{ck} \equiv \tilde{D}^{\mathrm{SD}}_{kc}$, $\tilde{t}_{aibj}$ (see Table III),
- precalculate the one-electron density $\tilde{D}^{\mathrm{SD}}_{pq}$, read $D^{(\mathrm{T})}_{ia}$ from disk and construct the one-electron density $D^{\mathrm{CCSD(T)}}_{pq}$
- loop over Δ (where Δ is a subset of basis functions belonging to the same shell and all symmetry related counterparts)
  - —loop over symmetrized AOs (SAO) $\delta \in \Delta$
    - –calculate the intermediates $t^{\delta}_{ai,j} = \Sigma_b t^{ab}_{ij} \Lambda^{h}_{\delta b}$, $\overline{t}^{\delta}_{ai,b} = \Sigma_b \overline{t^{ab}_{ij}} \Lambda^{h}_{\delta j}$, $Z^{\delta}_{ei,j} = \Sigma_{dk} \overline{t^{ed}_{ik}} t^{\delta}_{dk,j}$, and $\tilde{Z}^{\delta}_{ei,j} = \Sigma_{dk} t^{ed}_{ik} \tilde{t}^{\delta}_{dk,j}$,
    - –construct the first seven blocks of the one-index backtransformed density $\tilde{d}^{\mathrm{SD},\delta}_{pq,r}$ from the expressions given in Table III;
    - –construct from these blocks the two-index backtransformed density $\tilde{d}^{\mathrm{SD},\delta}_{pq,\gamma}$; construct the $\tilde{d}^{\mathrm{SD},\delta}_{abc}$ contribution to $\tilde{d}^{\mathrm{SD},\delta}_{ab\gamma}$ directly in an inner loop over γ;
    - –read $d^{(\mathrm{T}),\delta}_{pqr}$ from disk, backtransform r to γ and construct from the resulting blocks and $\tilde{d}^{\mathrm{SD},\delta}_{pq,\gamma}$ the CCSD(T) density $d^{\mathrm{CCSD(T)},\delta}_{pq,\gamma}$;
    - –add the frozen-core contributions listed in Tables II and IV;
    - –if necessary, backtransform remaining indices to AO basis within a loop over γ;
    - –if necessary, add relaxation contributions from $\overline{\kappa}$;
    - –for ${}^{\overline{\kappa}}\eta$ read in the undifferentiated integral distributions, transform the $\alpha\beta$ indices to MO and contract with the density;
    - –for F^{eff} contract $d_{\alpha\beta,\gamma\delta}$ with the undifferentiated two-electron integrals; for contraction with derivative integrals store $d_{\alpha\beta,\gamma\delta}$ on disk;
  - —end loop δ;
- end loop Δ.

In the current implementation of the CCSD(T) and CCSD gradients, the SD two-electron density is thus calculated twice—once to generate the right-hand side of the Z-vector equation ${}^{\overline{\kappa}}\eta$, and once to calculate the effective Fock matrix and the contribution to the gradient from the derivative integrals. An alternative approach, where the (nonseparable) two-electron density is calculated only once, can be developed using the methodology of Ref. 40.

TABLE III. The SD (and CCSD) densities in the Λ^h-backtransformed basis, where we have introduced the intermediates (Ref. 14): $\tilde{t}^{cd}_{kl} = 2t^{cd}_{kl} - t^{cd}_{lk}$; $\varepsilon_{ck} = \Sigma_{dl} \tilde{t}^{cd}_{kl} \overline{t}^{d}_{l}$; $t^{\delta}_{dk,j} = \Sigma_f t^{df}_{kj} \Lambda^{h}_{\delta f}$; $\tilde{t}^{\delta}_{dk,j} = \Sigma_f \tilde{t}^{df}_{kj} \Lambda^{h}_{\delta f}$; $Z^{\delta}_{ei,j} = \Sigma_{dk} \overline{t}^{ed}_{ik} t^{\delta}_{dk,j}$; $\tilde{Z}^{\delta}_{ei,j} = \Sigma_{dk} \overline{t}^{ed}_{ik} \tilde{t}^{\delta}_{dk,j}$; $\tilde{M}_{ijm,n} = \Sigma_{cd} t^{cd}_{jn} t^{cd}_{im}$; $X_{ij} = \Sigma_{cdk} t^{cd}_{ki} \tilde{t}^{cd}_{kj}$; $Y_{ab} = \Sigma_{ckl} t^{ca}_{kl} \tilde{t}^{cb}_{kl}$.

Correlated space

$$\tilde{d}^{\mathrm{SD},\delta}_{ijk} = 4\delta_{ij}\Lambda^{h}_{\delta k} - 2\delta_{kj}\Lambda^{h}_{\delta i} + 2\delta_{ij}\Sigma_a \varepsilon_{ak}\Lambda^{h}_{\delta a} - \delta_{kj}\Sigma_a \varepsilon_{ai}\Lambda^{h}_{\delta a} - \Sigma_e \tilde{t}^{\delta}_{ei,k}\overline{t}^{e}_{j} + \delta_{kj}\Sigma_l X_{il}\Lambda^{h}_{\delta l} - 2\delta_{ij}\Sigma_l X_{kl}\Lambda^{h}_{\delta l} - 2X_{ij}\Lambda^{h}_{\delta k} + X_{kj}\Lambda^{h}_{\delta i} + \Sigma_l \tilde{M}_{ijk,l}\Lambda^{h}_{\delta l}$$

$$\tilde{d}^{\mathrm{SD},\delta}_{ija} = 2\delta_{ij}\Sigma_k \overline{t}^{a}_{k}\Lambda^{h}_{\delta k} - \overline{t}^{a}_{j}\Lambda^{h}_{\delta i} + 2\delta_{ij}\Sigma_b Y_{ba}\Lambda^{h}_{\delta b} - \Sigma_{ck}\overline{t}^{ac}_{jk}t^{\delta}_{ck,i} - \Sigma_{ck}\overline{t}^{ca}_{jk}t^{\delta}_{ci,k}$$

$$\tilde{d}^{\mathrm{SD},\delta}_{aij} = 2\overline{t}^{a}_{i}\Lambda^{h}_{\delta j} - \delta_{ij}\Sigma_k \overline{t}^{a}_{k}\Lambda^{h}_{\delta k} - \delta_{ij}\Sigma_b Y_{ba}\Lambda^{h}_{\delta b} + \tilde{Z}^{\delta}_{ai,j}$$

$$\tilde{d}^{\mathrm{SD},\delta}_{aib} = \Sigma_j \overline{t}^{ab}_{ij}\Lambda^{h}_{\delta j}$$

$$\tilde{d}^{\mathrm{SD},\delta}_{iaj} = 2\varepsilon_{ai}\Lambda^{h}_{\delta j} - \varepsilon_{aj}\Lambda^{h}_{\delta i} - \Sigma_{ek}\tilde{t}^{ea}_{ji}\overline{t}^{e}_{k}\Lambda^{h}_{\delta k} + 2\tilde{t}^{\delta}_{ai,j} - \Sigma_e Y_{ae}\tilde{t}^{\delta}_{ei,j} - \Sigma_m X_{im}\tilde{t}^{\delta}_{am,j} - \Sigma_m X_{jm}\tilde{t}^{\delta}_{ai,m} - \Sigma_{bc}\tilde{t}^{ac}_{ij}Y_{bc}\Lambda^{h}_{\delta b} + \Sigma_{km}t^{\delta}_{am,k}\tilde{M}_{imjk} - \Sigma_{em}t^{ae}_{jm}\tilde{Z}^{\delta}_{em,i} + \Sigma_{em}t^{ea}_{jm}Z^{\delta}_{em,i} + \Sigma_{em}\tilde{t}^{ea}_{mi}\tilde{Z}^{\delta}_{em,j} + \Sigma_{ckem}t^{ac}_{kj}\tilde{t}^{ce}_{mk}t^{\delta}_{ei,m}$$

$$\tilde{d}^{\mathrm{SD},\delta}_{iab} = \Sigma_m \tilde{t}^{\delta}_{ai,m}\overline{t}^{b}_{m} - Y_{ab}\Lambda^{h}_{\delta i} + \Sigma_{dkj}\tilde{t}^{ad}_{ik}\overline{t}^{db}_{kj}\Lambda^{h}_{\delta j}$$

$$\tilde{d}^{\mathrm{SD},\delta}_{abi} = 2Y_{ba}\Lambda^{h}_{\delta i} + \Sigma_m \overline{t}^{a}_{m}\tilde{t}^{\delta}_{bm,i} - \Sigma_{ckj}t^{cb}_{ki}\overline{t}^{ca}_{kj}\Lambda^{h}_{\delta j} - \Sigma_{ckj}t^{cb}_{ik}\overline{t}^{ca}_{jk}\Lambda^{h}_{\delta j}$$

$$\tilde{d}^{\mathrm{SD},\delta}_{abc} = \Sigma_{mn}t^{\delta}_{bm,n}\overline{t}^{ac\ a}_{mn}$$

[a]To avoid an expensive backtransformation of the c index to AO, the given contribution is calculated directly with two indices in the AO basis as $\tilde{d}^{\mathrm{SD},\delta\gamma}_{ab} = \Sigma_{mn}t^{\delta}_{bm,n}\overline{t}^{\gamma}_{am,n}$ within an inner loop over γ.

TABLE IV. The symmetry-unique blocks of the two-electron (T) density in the regular MO basis. The permutation operators P^{ab}_{ij} and P^{TCME}_{aibj} are defined in Eqs. (58) and (59), respectively.

Correlated space

$$d^{(\mathrm{T})}_{iajb} = P^{\mathrm{TCME}}_{aibj}P^{ab}_{ij}\Sigma_{dl}(t^{abd}_{ijl} - t^{abd}_{lji})t^{*d}_{l}$$

$$d^{(\mathrm{T})}_{iajk} = -2\Sigma_{dle}(2t^{dea}_{lji} - t^{dea}_{ijl} - t^{dea}_{lij})t^{*de}_{lk} + 2\Sigma_{dlem}[2\delta_{jk}(t^{dea}_{lmi} - t^{dea}_{lim}) - \delta_{ik}(t^{dea}_{lmj} - t^{dea}_{ljm})]t^{*de}_{lm}$$

$$d^{(\mathrm{T})}_{aijk} = -\Sigma_{dle}\overline{t}^{dea}_{lki}t^{de}_{lj}$$

$$d^{(\mathrm{T})}_{abci} = -\Sigma_{dlm}\overline{t}^{dac}_{lmi}t^{db}_{lm}$$

$$d^{(\mathrm{T})}_{abic} = 2\Sigma_{dlm}(2t^{dcb}_{lim} - t^{dcb}_{lmi} - t^{dcb}_{ilm})t^{*da}_{lm}$$

Additional frozen-core terms

$$d^{(\mathrm{T})}_{iaJK} = 2\delta_{JK}D^{(\mathrm{T})}_{ia}$$

$$d^{(\mathrm{T})}_{iajK} = -\delta_{IK}D^{(\mathrm{T})}_{ja}$$

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

D. The right-hand side of the orbital-rotation multiplier equations within the integral-density direct algorithm

The general expression for the right-hand side vector for the *Z*-vector equations in terms of the one- and two-electron density matrices was given in Eq. (50). For an integral-density direct formulation, we transform two indices in the two-electron contribution to the AO basis:

$$\bar{\kappa}\eta_{pq}^{\mathrm{CCSD(T)}}=(1-P_{pq})\Bigg\{\sum_{t}(D_{tq}^{\mathrm{CCSD(T)}}+D_{qt}^{\mathrm{CCSD(T)}})h_{pt}+\sum_{t\gamma\delta}(d_{tq,\gamma\delta}^{\mathrm{CCSD(T)}}+d_{qt,\gamma\delta}^{\mathrm{CCSD(T)}})g_{pt,\gamma\delta}\Bigg\}. \tag{69}$$

Within the scheme described at the beginning of Sec. III, this equation is implemented as follows: Within a loop over δ, the $\tilde{d}_{pq,r}^{\mathrm{SD},\delta}$ is calculated on the fly, and the various blocks of $d_{pq,r}^{(\mathrm{T}),\delta}$ are read from disk. For both densities, the r index is backtransformed to the AO basis to obtain $\tilde{d}_{pq\gamma}^{\mathrm{SD},\delta}$, $d_{pq\gamma}^{(\mathrm{T}),\delta}$ and finally $d_{pq\gamma}^{\mathrm{CCSD(T)},\delta}$. The integrals $g_{\alpha\beta\gamma}^{\delta}$ (calculated in the loop over Δ) are read into memory, partially transformed to the MO basis in a loop over γ, and contracted with the two-electron densities.

Note that, in the CCSD case, the occupied–occupied and virtual–virtual blocks of $\bar{\kappa}\eta$ are not required since the CCSD energy is invariant to orbital rotations among the occupied orbitals or among the virtual orbitals. The explicit expressions for the symmetry-unique blocks of the right-hand sides of the orbital-rotation multipliers are collected in Tables V and VI, for the SD and (T) parts, respectively.

E. The diagonal orbital-rotation multipliers

The diagonal orbital-rotation multipliers originate exclusively from the triples space:

$$\bar{\kappa}_{pp}=\sum_{\mu_3}\bar{t}_{\mu_3}\langle\mu_3|[E_{pp},T_3]|\mathrm{HF}\rangle. \tag{70}$$

For $p=a$ and $p=i$, in particular, we obtain

$$\bar{\kappa}_{aa}=\frac{1}{2}\sum_{ckdlm}\bar{t}_{klm}^{cda}t_{klm}^{cda}, \tag{71}$$

$$\bar{\kappa}_{ii}=-\frac{1}{2}\sum_{ckdle}\bar{t}_{kli}^{cde}t_{kli}^{cde}. \tag{72}$$

These multipliers cannot be calculated using the *S* and *Q* intermediates of Ref. 48. Instead, we need to introduce another intermediate

$$U^{ab}(ckji)=-\frac{1}{\epsilon_{ijk}^{abc}}\tilde{X}_{ijk}^{abc} \tag{73}$$

such that a triples amplitude or multiplier can be rewritten as

$$X_{ijk}^{abc}=-\frac{1}{\epsilon_{ijk}^{abc}}P_{ijk}^{abc}(\tilde{X}_{ijk}^{abc})=P_{jk}^{bc}\{S^{bc}(aikj)+U^{bc}(aikj)\}. \tag{74}$$

TABLE V. Explicit expressions for the symmetry unique blocks of the SD (and CCSD) right-hand sides of the orbital-rotation multiplier equations within the correlated space in terms of densities and integrals in the Λ^p, Λ^h-basis. Note that the occupied-occupied and virtual-virtual blocks are not required in the CCSD case. In the frozen core approximation a few contributions must be added to each block, which are obtainable from the equations below letting the summation indices over occupied orbitals refer to frozen orbitals. The additional blocks $\bar{\kappa}\eta_{aI}^{\mathrm{SD}}$ and $\bar{\kappa}\eta_{iJ}^{\mathrm{SD}}$ are also required, which can be easily derived from the formulas given here and the recipe in Sec. III G.

$$\begin{aligned}\bar{\kappa}\eta_{ai}^{\mathrm{SD}}=&\Sigma_t(\hat{h}_{ta}\tilde{D}_{ti}^{\mathrm{SD}}-\hat{h}_{it}\tilde{D}_{at}^{\mathrm{SD}}-\hat{h}_{ti}\tilde{D}_{ta}^{\mathrm{SD}}+\hat{h}_{at}\tilde{D}_{it}^{\mathrm{SD}})\\&-\Sigma_{tj}t_{aj}(\hat{h}_{ti}\tilde{D}_{tj}^{\mathrm{SD}}-\hat{h}_{jt}\tilde{D}_{it}^{\mathrm{SD}})+\Sigma_{tb}t_{bi}(\hat{h}_{tb}\tilde{D}_{ta}^{\mathrm{SD}}-\hat{h}_{at}\tilde{D}_{bt}^{\mathrm{SD}})\\&+\Sigma_{tbj}t_{aj}t_{bi}(\hat{h}_{tb}\tilde{D}_{tj}^{\mathrm{SD}}-\hat{h}_{jt}\tilde{D}_{bt}^{\mathrm{SD}})+\Sigma_{trs}(\hat{g}_{tars}\tilde{d}_{tirs}^{\mathrm{SD}}\\&-\hat{g}_{itrs}\tilde{d}_{atrs}^{\mathrm{SD}}-\hat{g}_{tirs}\tilde{d}_{tars}^{\mathrm{SD}}+\hat{g}_{atrs}\tilde{d}_{itrs}^{\mathrm{SD}})-\Sigma_{trsj}t_{aj}(\hat{g}_{tirs}\tilde{d}_{tjrs}^{\mathrm{SD}}-\hat{g}_{jtrs}\tilde{d}_{itrs}^{\mathrm{SD}})\\&+\Sigma_{tbrs}t_{bi}(\hat{g}_{tbrs}\tilde{d}_{tars}^{\mathrm{SD}}-\hat{g}_{atrs}\tilde{d}_{btrs}^{\mathrm{SD}})+\Sigma_{tbjrs}t_{aj}t_{bi}(\hat{g}_{tbrs}\tilde{d}_{tjrs}^{\mathrm{SD}}-\hat{g}_{jtrs}\tilde{d}_{btrs}^{\mathrm{SD}})\end{aligned}$$

$$\begin{aligned}\bar{\kappa}\eta_{ab}^{\mathrm{SD}}=&(1-P_{ab})\{\Sigma_t(\hat{h}_{ta}\tilde{D}_{tb}^{\mathrm{SD}}+\hat{h}_{at}\tilde{D}_{bt}^{\mathrm{SD}})+\Sigma_t\Sigma_j t_{bj}(\hat{h}_{ta}\tilde{D}_{tj}^{\mathrm{SD}}-\hat{h}_{jt}\tilde{D}_{at}^{\mathrm{SD}})\\&+\Sigma_{trs}(\hat{g}_{tars}\tilde{t}_{tbrs}^{\mathrm{SD}}+\hat{g}_{atrs}\tilde{d}_{btrs}^{\mathrm{SD}})+\Sigma_{trs}\Sigma_j t_{bj}(\hat{g}_{tars}\tilde{d}_{tjrs}^{\mathrm{SD}}-\hat{g}_{jtrs}\tilde{d}_{atrs}^{\mathrm{SD}})\}\end{aligned}$$

$$\begin{aligned}\bar{\kappa}\eta_{ij}^{\mathrm{SD}}=&(1-P_{ij})\{\Sigma_t(\hat{h}_{ti}\tilde{D}_{tj}^{\mathrm{SD}}+\hat{h}_{it}\tilde{D}_{jt}^{\mathrm{SD}})+\Sigma_t\Sigma_c t_{cj}(\hat{h}_{tc}\tilde{D}_{ti}^{\mathrm{SD}}-\hat{h}_{it}\tilde{D}_{ct}^{\mathrm{SD}})\\&+\Sigma_{trs}(\hat{g}_{tirs}\tilde{d}_{tjrs}^{\mathrm{SD}}+\hat{g}_{itrs}\tilde{d}_{jtrs}^{\mathrm{SD}})+\Sigma_{trs}\Sigma_c t_{cj}(\hat{g}_{tcrs}\tilde{d}_{tirs}^{\mathrm{SD}}-\hat{g}_{itrs}\tilde{d}_{ctrs}^{\mathrm{SD}})\}\end{aligned}$$

The diagonal orbital-rotation multipliers can then be calculated as

$$\begin{aligned}\bar{\kappa}_{aa}=&\frac{1}{2}\sum_{ckdln}P_{kl}^{cd}\{\bar{S}^{cd}(anlk)+\bar{U}^{cd}(anlk)\}\\&\times P_{kl}^{cd}\{S^{cd}(anlk)+U^{cd}(anlk)\}\\=&\sum_{ckdln}\{\bar{S}^{cd}(anlk)+\bar{U}^{cd}(anlk)\}\\&\times P_{kl}^{cd}\{S^{cd}(anlk)+U^{cd}(anlk)\},\end{aligned} \tag{75}$$

TABLE VI. Explicit expressions for the symmetry-unique blocks of the (T) right-hand side of the orbital-rotation multiplier equations in the regular MO basis, within the correlated space. In the frozen core approximation a few contributions must be added to each block, obtainable from the expressions below by letting the summation indices over occupied orbitals refer to frozen orbitals. The additional blocks $\bar{\kappa}\eta_{aI}^{(\mathrm{T})}$ and $\bar{\kappa}\eta_{iJ}^{(\mathrm{T})}$ are also required, which can be easily derived from the formulas given here and the recipe in Sec. III G.

$$\begin{aligned}\bar{\kappa}\eta_{ai}^{(\mathrm{T})}=&\Sigma_b h_{ab}D_{ib}^{(\mathrm{T})}-\Sigma_j h_{ji}D_{ja}^{(\mathrm{T})}+\Sigma_{lcm}[{}^{S}d_{limc}^{(\mathrm{T})}+{}^{S}d_{ilmc}^{(\mathrm{T})}]g_{lamc}\\&-\Sigma_{fcm}[{}^{S}d_{famc}^{(\mathrm{T})}+{}^{S}d_{afmc}^{(\mathrm{T})}]g_{fimc}-\Sigma_{lmn}[d_{lamn}^{(\mathrm{T})}\\&+d_{almn}^{(\mathrm{T})}]g_{limn}-\Sigma_{lcm}[d_{lamc}^{(\mathrm{T})}]g_{licm}-\Sigma_{lcd}[d_{lacd}^{(\mathrm{T})}\\&+d_{alcd}^{(\mathrm{T})}]g_{licd}+\Sigma_{fmn}[d_{fimn}^{(\mathrm{T})}+d_{ifmn}^{(\mathrm{T})}]g_{famn}\\&+\Sigma_{fcd}[d_{ficd}^{(\mathrm{T})}+d_{ifcd}^{(\mathrm{T})}]g_{facd}+\Sigma_{fcm}[d_{ifmc}^{(\mathrm{T})}]g_{famc}\end{aligned}$$

$$\begin{aligned}\bar{\kappa}\eta_{ij}^{(\mathrm{T})}=&(1-P_{ij})\{\Sigma_c h_{ic}D_{jc}^{(\mathrm{T})}+\Sigma_{cmn}[{}^{S}d_{njmc}^{(\mathrm{T})}+{}^{S}d_{jnmc}^{(\mathrm{T})}]g_{nimc}\\&+\Sigma_{lmc}[d_{cjlm}^{(\mathrm{T})}+d_{jclm}^{(\mathrm{T})}]g_{cilm}+\Sigma_{ldc}[d_{jcld}^{(\mathrm{T})}]g_{cild}\\&+\Sigma_{fdc}[d_{cjfd}^{(\mathrm{T})}+d_{jcfd}^{(\mathrm{T})}]g_{cifd}\}\end{aligned}$$

$$\begin{aligned}\bar{\kappa}\eta_{ab}^{(\mathrm{T})}=&(1-P_{ab})\{\Sigma_j h_{ja}D_{jb}^{(\mathrm{T})}+\Sigma_{nml}[d_{lbnm}^{(\mathrm{T})}+d_{blnm}^{(\mathrm{T})}]g_{lanm}\\&+\Sigma_{mcl}[d_{lbmc}^{(\mathrm{T})}]g_{lamc}+\Sigma_{dcl}[d_{lbdc}^{(\mathrm{T})}+d_{blac}^{(\mathrm{T})}]g_{ladc}\\&+\Sigma_{dcl}[{}^{S}d_{cbld}^{(\mathrm{T})}+{}^{S}d_{bcld}^{(\mathrm{T})}]g_{cald}\}\end{aligned}$$

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

TABLE VII. Equilibrium CCSD(T) bond lengths (in Å) of the cyclic **2s** isomer of SiC_3. C* indicates the transannular carbon atoms; ''fc'' stands for ''frozen-core approximation'' and ''all'' for ''all electrons correlated.'' The number in square parentheses corresponds to the number of contracted basis functions in the given basis set.

	cc-pVQZ/fc [224]	cc-pV5Z/fc [368]	cc-pwCVQZ(Si)/ cc-pCVQZ(C)/all[a] [361]
$r_{\text{Si-C*}}$	1.8393	1.8359	1.8290
$r_{\text{C-C*}}$	1.4381	1.4370	1.4342
$r_{\text{C*-C*}}$	1.4902	1.4887	1.4830

[a]From Ref. 50.

$$\begin{aligned}\overline{\kappa}_{ii} &= -\frac{1}{2}\sum_{ckdle} P_{kl}^{cd}\{\overline{S}^{cd}(eilk)+\overline{U}^{cd}(eilk)\} \\ &\quad\times P_{kl}^{cd}\{S^{cd}(eilk)+U^{cd}(eilk)\} \\ &= -\sum_{ckdle}\{\overline{S}^{cd}(eilk)+\overline{U}^{cd}(eilk)\}P_{kl}^{cd}\{S^{cd}(eilk) \\ &\quad + U^{cd}(eilk)\}. \end{aligned} \tag{76}$$

We thus need to calculate the S and U intermediates for both combinations of the two fixed summation indices, which means that we will have OV^4 I/O in comparison with OV^3 for the ground-state energy calculation. For a more thorough discussion of the implementation, see Ref. 48.

F. The CCSD(T) geometrical gradient in the integral-density direct algorithm

A demanding step in the gradient calculation is the contraction of the two-electron densities with the derivative two-electron integrals to the contribution

$$L^{[1]}(2e) = \frac{1}{2}\sum_{\alpha\beta\gamma\delta} g^{[1]}_{\alpha\beta\gamma\delta} d^{\text{eff}}_{\alpha\beta\gamma\delta}. \tag{77}$$

Already the storage of the full undifferentiated AO integrals $g_{\alpha\beta\gamma\delta}$ poses serious limitations to the applicability for large systems, unless direct techniques are used. Even more so, any approach where the derivative AO integrals are precalculated and stored on disk is highly impractical even for systems of moderate size, since it would require an order of magnitude more disk space with no reduction in the operation count.

The algorithm adopted in the present implementation still assumes that $d^{\text{eff}}_{\alpha\beta\gamma\delta}$ is calculated in a loop over the AO index δ for all α, β, γ. Since an efficient integral evaluation requires that all derivative integrals with AO indices δ belonging to the same shell and all symmetry-related counterparts are calculated simultaneously, and since we cannot store a complete batch of the differentiated integrals $g^{[1],\delta}_{\alpha\beta\gamma}$ for all α, β, γ in memory, we have developed the following scheme, where the two-electron density is accumulated in three-index batches on disk, read back in two-index batches, and contracted with differentiated integrals calculated on the fly:

- loop over Δ (where Δ is a subset of basis functions belonging to the same shell and all symmetry related counterparts)
  - —loop over SAOs $\delta\in\Delta$
    calculated $d^{\text{eff}}_{\alpha\beta\gamma\delta}$ for all α,β,γ
    store $d^{\text{eff}}_{\alpha\beta\gamma\delta}$ on disk
  - —end loop δ
  - —loop over Γ (where Γ is similar subset of basis functions as Δ)
    read $d^{\text{eff}}_{\alpha\beta\gamma\delta}\forall\alpha$, β and $\forall\gamma\in\Gamma$, $\delta\in\Delta$
    calculate $g^{[x]}_{\alpha\beta\gamma\delta}\forall\alpha$, β and $\forall\gamma\in\Gamma$, $\delta\in\Delta$ and all necessary directions x (12 at most)
    contract density and integrals to $L^{[x]}(2e) = \frac{1}{2}\Sigma_{\alpha\beta\gamma\delta} g^{[x]}_{\alpha\beta\gamma\delta} d^{\text{eff}}_{\alpha\beta\gamma\delta}$
  - —end loop Γ
- end loop Δ

In this way, we keep the memory and disk space requirements essentially down to what is needed for the calculation of the density d^{eff}. The additional disk space needed for the out-of-core treatment of the density is $\mathcal{O}(N^3)$ and the additional I/O introduced is $\mathcal{O}(N^4)$. The strategy used for the efficient evaluation of the two-electron derivative integrals is outlined in Sec. IV.

G. Implementation of the frozen-core approximation

When introducing frozen-core orbitals, we divide the orbitals into three sets: frozen occupied $(I,J,K,L,\ldots)$, active occupied $(i,j,k,l,\ldots)$, and active virtual $(a,b,c,d,\ldots)$. As shown in Ref. 3, the criterion for frozen-core orbitals is that the Fock matrix does not have an interaction between the frozen and the active subspaces:

$$F_{Ii} = F_{iI} = 0, \tag{78}$$

$$F_{Ia} = F_{aI} = 0. \tag{79}$$

These constraints have to be incorporated in our Lagrange function in Eq. (18). In the canonical representation, however, these criteria are already fulfilled since the Fock matrix is diagonal, implying that the multipliers $\overline{\kappa}$ fulfill an even stricter criterion. The frozen-core approximation—where the frozen orbitals correspond to the innermost HF (canonical) orbitals—may therefore be implemented by the use of the ''nonfrozen orbital'' Lagrange function with the canonical condition as a constraint, and letting the amplitudes and multipliers only refer to active orbitals. By contrast, the $\overline{\kappa}\eta$ vector, the densities, and the integrals may possess indices that refer to inactive orbitals.

Having obtained a result without the frozen-core approximation (but in the canonical representation), the (additional) frozen-core terms can easily be obtained as discussed above. As an example, we consider the $\tilde{d}^{\text{SD}}_{ijab}$ density in Table II. Except for the term with the Kronecker delta, all indices refer to either amplitudes or multipliers. The only frozen-core contribution is thus

$$\tilde{d}^{\text{SD}}_{IJab} = 2\,\delta_{IJ}\sum_{ckl} \overline{t}^{ca}_{kl} t^{cb}_{kl}. \tag{80}$$

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

Remember that particle symmetry is fulfilled for two-electron quantities, meaning that $\tilde{d}^{\mathrm{SD}}_{abIJ}$ is identical to $\tilde{d}^{\mathrm{SD}}_{IJab}$. The frozen-core additional MO contributions to the one- and two-electron densities are given in Tables I, II, and IV. The various blocks of the $\bar{\kappa}\eta_{pq}$ vector within the frozen-core approximation can be derived from the expressions in Table V and VI, allowing the indices for the occupied orbitals to refer to both frozen and correlated orbitals. This leads to five unique blocks: $\bar{\kappa}\eta_{ai}$, $\bar{\kappa}\eta_{ij}$, $\bar{\kappa}\eta_{ab}$, $\bar{\kappa}\eta_{iJ}$ and $\bar{\kappa}\eta_{aI}$. There are no frozen-core contributions to the diagonal orbital-rotation multipliers.

IV. INTEGRAL EVALUATION

Let us briefly consider the evaluation of integrals over differentiated solid-harmonic Gaussian-type orbitals (GTOs). For the calculation of CCSD and CCSD(T) gradients, we have made a new implementation of derivative integrals in DALTON,[46] as required for our integral-density direct formulation of gradients. In this implementation, we avoid the separate transformation first from undifferentiated Cartesian GTOs to differentiated Cartesian GTOs and next to differentiated solid-harmonic GTOs. Instead, we carry out the transformation in a single step, expanding the differentiated solid-harmonic GTOs directly in undifferentiated Cartesian GTOs. This approach is particularly useful for high-angular momentum functions, reducing the cost of the integration.

We apply the McMurchie–Davidson scheme,[25,49] in which the primary integrals are generated over undifferentiated Cartesian Gaussians of the form

$$G_{ijk}(\mathbf{r},\alpha,\mathbf{A}) = x_A^i y_A^j z_A^k \exp(-\alpha r_A^2), \tag{81}$$

with $i \geqslant 0$, $j \geqslant 0$, and $k \geqslant 0$. During the calculation, Cartesian Gaussians are transformed into solid-harmonic form

$$G_{lm}(\mathbf{r},\alpha,\mathbf{A}) = S_{lm}(x_A,y_A,z_A)\exp(-\alpha r_A^2) \tag{82}$$

with $l \geqslant |m| \geqslant 0$ by means of the transformation

$$G_{lm}(\mathbf{r},\alpha,\mathbf{A}) = N_{lm} \sum_{t=0}^{\lfloor l-|m|/2 \rfloor} \sum_{u=0}^{t} \sum_{v=v_m}^{\lfloor |m|/2-v_m \rfloor + v_m} C_{tuv}^{lm} \times G_{|m|+2(t-u-v),2(u+v),l-|m|-2t}(\mathbf{r},\alpha,\mathbf{A}), \tag{83}$$

where

$$N_{lm} = \frac{1}{2^{|m|} l!} \sqrt{\frac{2(l+|m|)!(l-|m|)!}{2^{\delta_{0m}}}}, \tag{84}$$

$$C_{tuv}^{lm} = (-1)^{t+v-v_m} \left(\frac{1}{4}\right)^t \binom{l}{t} \binom{l-t}{|m|+t} \binom{t}{u} \binom{|m|}{2v}, \tag{85}$$

$$v_m = \begin{cases} 0 & \text{if } m \geqslant 0 \\ \frac{1}{2} & \text{if } m < 0 \end{cases}. \tag{86}$$

Since the number of solid-harmonic Gaussians is smaller than the number of Cartesian Gaussians, this transformation is carried out as early as possible in the course of the integration.

To evaluate derivatives of solid-harmonic Gaussians, we first note that differentiated Gaussians are simple linear combinations of undifferentiated Gaussians:

$$\frac{\mathrm{d}G_{ijk}(\mathbf{r},\alpha,\mathbf{A})}{\mathrm{d}A_x} = 2\alpha G_{i+1,j,k}(\mathbf{r},\alpha,\mathbf{A}) - iG_{i-1,j,k}(\mathbf{r},\alpha,\mathbf{A}). \tag{87}$$

It should therefore be possible to generalize the transformation Eq. (83) to the expansion of differentiated solid-harmonic Gaussians in terms of undifferentiated Cartesian Gaussians. Such an expansion, valid to all orders, is given by

$$\begin{aligned} \frac{\mathrm{d}^{i+j+k}G_{lm}(\mathbf{r},\alpha,\mathbf{A})}{\mathrm{d}A_x^i\,\mathrm{d}A_y^j\,\mathrm{d}A_z^k} = N_{lm} \sum_{t=0}^{\lfloor l-|m|/2 \rfloor} \sum_{u=0}^{t} \sum_{v=v_m}^{\lfloor |m|/2-v_m \rfloor + v_m} C_{tuv}^{lm} \sum_{a=0}^{i} \sum_{b=0}^{j} \sum_{c=0}^{k} D_{tuvabc}^{lm} \\ \times \sum_{p=0}^{\lfloor i-a/2 \rfloor} E_{ap}^i \sum_{q=0}^{\lfloor j-b/2 \rfloor} E_{bq}^j \sum_{r=0}^{\lfloor k-c/2 \rfloor} E_{cr}^k \alpha^{i+j+k-a-b-c-p-q-r} \\ \times G_{i-2(a+p)+|m|+2(t-u-v),j-2(b+q)+2(u+v),k-2(c+r)+l-|m|-2t}(\mathbf{r},\alpha,\mathbf{A}), \end{aligned} \tag{88}$$

where we have introduced

$$D_{tuvabc}^{lm} = (|m|+2t-2u-2v-a+1)_a \times (2u+2v-b+1)_b (l-|m|-2t-c+1)_c, \tag{89}$$

$$E_{ap}^i = \frac{(-1)^{a+p} 2^{i-a-2p} i!}{a!p!(i-a-2p)!}, \tag{90}$$

and $(x)_n = x(x+1)\cdots(x+n-1)$. The linear transformation Eq. (88) may be implemented and carried out in the same manner as the transformation to undifferentiated solid-harmonic Gaussians Eq. (83), except that the integrals must be scaled by some power of α prior to the transformation. In our implementation, we begin by precalculating the α-independent coefficients from Eq. (88), setting up the necessary (sparse) matrices (one matrix for each *lm* and *ijk*) that are later used for the transformation from undifferentiated Cartesian GTOs to differentiated solid-harmonic GTOs. Since the transformation matrices are independent of α, the transformation to derivative solid-harmonic GTOs may be carried out after the transformation from primitive to contracted GTOs (if the primitive GTOs are scaled by α before contraction).

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

V. RESULTS

As an illustrative application of the new integral-density direct analytic CCSD(T) gradient, we have carried out a geometry optimization of the **2s** cyclic isomer of SiC_3. The SiC_3 isomers have been the subject of several recent studies, aimed to determine the most stable isomer and its equilibrium geometry.[50–52] The most accurate result is the CCSD(T)/cc-pwCVQZ (cc-pCVQZ for C) result obtained by Stanton, Gauss, and Christiansen[50] by numerical geometry optimization with all 32 electrons correlated. We have reoptimized the geometry at the CCSD(T)/cc-pVQZ and cc-pV5Z levels, keeping the $1s$, $2s$, and $2p$ orbitals of Si and the $1s$ orbital of C frozen during the optimization. This corresponds to an analytic CCSD(T) optimization with 16 correlated electrons in a basis of 224 and 368 contracted functions for cc-pVQZ and cc-pV5Z, respectively. The results are given in Table VII. By comparing the numerical all-electron core-valence results of Stanton *et al.*[50] with our frozen-core results, we can estimate the importance of core correlation.

Comparing the cc-pVQZ and the cc-pwCVQZ(Si)/cc-pCVQZ(C) results, see Table VII, we find that the inclusion of core correlation leads to a small contraction of the bonds of the order of 0.2%–0.5%. The extension of the basis set from quadruple- to quintuple-zeta also leads to a slight (but less pronounced) contraction, and the differences between the cc-pV5Z/frozen-core and cc-pwCQZ/cc-pCVQZ/all-electrons results are of the order of 0.2%–0.4%. However, this modest loss of accuracy is more than compensated by the saving in computational cost of about 80%, considering the $\mathcal{O}(O^3V^4)$ bottleneck of the CCSD(T) approach.

VI. CONCLUSION

We have presented a novel, integral-density direct implementation of the analytic CCSD(T) gradient, based on the Lagrangian formulation of the CCSD(T) energy. The CCSD gradient has been obtained as a subset of the CCSD(T) gradient. Using the canonical condition for the HF orbitals, the treatment of frozen orbitals has been incorporated into the CCSD and CCSD(T) gradient at a general, abstract level. The frozen-core approximation is important for reducing the number of excitations for systems with a large number of electrons, thus extending the applicability of the CCSD(T) method to larger systems. For molecules containing second-row elements, the use the frozen-core approximation is almost mandatory since core-valence basis sets are in general not available and, if they were, the calculation would be too expensive. Furthermore, all-electron calculations using valence basis sets may have large errors in the treatment of the core electrons.

As a preliminary application, we have considered the geometry optimization of the c-SiC_3 (**2s**) isomer at the cc-pVQZ and cc-pV5Z levels with only the valence electrons correlated, allowing us to estimate the importance of core correlation by comparison with the numerical results of Stanton, Gauss, and Christiansen.[50] A systematic and detailed investigation of the effect of core correlation on bond lengths and bond angles of small and medium-sized molecules containing second-row elements will be presented in a separate communication. With the present CCSD(T) frozen-core implementation of the molecular gradient, geometry optimizations for systems with 5–10 atoms in triple-zeta basis sets have become routine, and systems containing as many as 20 atoms may be studied in special cases.

ACKNOWLEDGMENTS

This work has been supported by the Danish Research Council (Grant No. 9901973) and by the European Research and Training Network: ''Molecular Properties and Molecular Materials'' (MOLPROP), Contract No. HPRN-CT-2000-00013. S.C. acknowledges support from the Italian Ministero dell'Istruzione, Università e Ricerca (MIUR), Programmi di ricerca di interesse nazionale (COFIN2000).

[1] T. Helgaker and P. Jørgensen, in *Methods in Computational Molecular Physics*, edited by S. Wilson and G. H. F. Diercksen (Plenum, New York, 1992).
[2] P. Pulay, in *Modern Electronic Structure Theory, Part II*, edited by D. R. Yarkony (World Scientific, Singapore, 1995).
[3] H. Koch, H. J. Aa. Jensen, P. Jørgensen, T. Helgaker, G. E. Scuseria, and H. F. Schaefer III, J. Chem. Phys. **92**, 4924 (1990).
[4] A. C. Scheiner, G. E. Scuseria, J. E. Rice, T. J. Lee, and H. F. Schaefer III, J. Chem. Phys. **87**, 3539 (1987).
[5] G. E. Scuseria, J. Chem. Phys. **94**, 442 (1991).
[6] J. Gauss, J. F. Stanton, and R. J. Bartlett, J. Chem. Phys. **95**, 2623 (1991).
[7] J. Gauss, J. F. Stanton, and R. J. Bartlett, J. Chem. Phys. **95**, 2639 (1991).
[8] J. Gauss, W. J. Lauderdale, J. F. Stanton, J. D. Watts, and R. J. Bartlett, Chem. Phys. Lett. **182**, 207 (1991).
[9] A. P. Rendell and T. J. Lee, J. Chem. Phys. **94**, 6219 (1991).
[10] T. J. Lee and A. P. Rendell, J. Chem. Phys. **94**, 6229 (1991).
[11] J. D. Watts, J. Gauss, and R. J. Bartlett, Chem. Phys. Lett. **200**, 1 (1993).
[12] J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).
[13] J. Gauss and J. F. Stanton, J. Chem. Phys. **104**, 2574 (1996).
[14] A. Halkier, H. Koch, O. Christiansen, P. Jørgensen, and T. Helgaker, J. Chem. Phys. **107**, 849 (1997).
[15] H. Koch, O. Christiansen, R. Kobayashi, P. Jørgensen, and T. Helgaker, Chem. Phys. Lett. **228**, 233 (1994).
[16] H. Koch, A. S. de Meras, T. Helgaker, and O. Christiansen, J. Chem. Phys. **104**, 4157 (1996).
[17] M. Schütz, R. Lindh, and H.-J. Werner, Mol. Phys. **96**, 719 (1999).
[18] G. D. Purvis and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
[19] J. Noga and R. J. Bartlett, J. Chem. Phys. **86**, 7041 (1987).
[20] J. Noga and R. J. Bartlett, J. Chem. Phys. **89**, 3401 (1988).
[21] G. E. Scuseria and H. F. Schaefer III, Chem. Phys. Lett. **152**, 382 (1988).
[22] R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, Chem. Phys. Lett. **165**, 513 (1990).
[23] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[24] T. H. Dunning, Jr., J. Phys. Chem. A **104**, 9062 (2000).
[25] T. Helgaker, P. Jørgensen and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, Chichester, 2000).
[26] T. Helgaker, J. Gauss, P. Jørgensen, and J. Olsen, J. Chem. Phys. **106**, 6430 (1997).
[27] A. Halkier, P. Jørgensen, J. Gauss, and T. Helgaker, Chem. Phys. Lett. **274**, 235 (1997).
[28] K. L. Bak, J. Gauss, P. Jørgensen, J. Olsen, T. Helgaker, and J. F. Stanton, J. Chem. Phys. **114**, 6548 (2001).
[29] A. Halkier and P. R. Taylor, Chem. Phys. Lett. **285**, 133 (1998).
[30] K. L. Bak, J. Gauss, T. Helgaker, P. Jørgensen, and J. Olsen, Chem. Phys. Lett. **319**, 563 (2000).
[31] A. Halkier, S. Coriani, and P. Jørgensen, Chem. Phys. Lett. **294**, 292 (1998).
[32] S. Coriani, A. Halkier, A. Rizzo, and K. Ruud, Chem. Phys. Lett. **326**, 269 (2000).
[33] K. L. Bak, P. Jørgensen, J. Olsen, T. Helgaker, and W. Klopper, J. Chem. Phys. **112**, 9229 (2000).
[34] T. H. Dunning, Jr., K. A. Peterson and D. E. Woon, in *Encyclopedia of Computational Chemistry*, edited by P. v. R. Schleyer, N. L. Allinger,

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp

T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, and P. R. Schreiner (Wiley, Chichester, 1998), Vol. 1, p. 88.
[35] J. M. L. Martin, T. J. Lee, and P. R. Taylor, J. Chem. Phys. **97**, 8361 (1992).
[36] J. M. L. Martin, P. R. Taylor, and T. J. Lee, Chem. Phys. Lett. **205**, 535 (1993).
[37] T. J. Lee, J. M. L. Martin, and P. R. Taylor, J. Chem. Phys. **102**, 254 (1995).
[38] J. M. L. Martin and P. R. Taylor, Spectrochim. Acta, Part A **53**, 1039 (1997).
[39] J. M. L. Martin, T. J. Lee, and P. R. Taylor, J. Chem. Phys. **108**, 676 (1998).
[40] F. Haase and R. Ahlrichs, J. Comput. Chem. **14**, 907 (1993).
[41] A. E. Azhary, G. Rauhut, P. Pulay, and H.-J. Werner, J. Chem. Phys. **10**, 5185 (1993).
[42] P. Pulay, S. Sæbø, and W. Meyer, J. Chem. Phys. **1901**, 719 (1984).
[43] T. Helgaker and P. Jørgensen, Theor. Chim. Acta **75**, 111 (1989).
[44] O. Christiansen, H. Koch, A. Halkier, P. Jørgensen, T. Helgaker, and A. S. de Meras, J. Chem. Phys. **105**, 6921 (1996).
[45] P. Jørgensen and T. Helgaker, J. Chem. Phys. **89**, 1560 (1988).
[46] T. Helgaker, H. J. A. Jensen, P. Jørgensen *et al.* DALTON, an *ab initio* electronic structure program, Release 1.2, 2001. See http://www.kjemi.uio.no/software/dalton/dalton.html
[47] A. Halkier, Ph.D. thesis, Aarhus University, Århus, Denmark, July 1999.
[48] K. Hald, P. Jørgensen, O. Christiansen, and H. Koch, J. Chem. Phys. **116**, 5963 (2002).
[49] L. E. McMurchie and E. R. Davidson, J. Comput. Phys. **26**, 218 (1978).
[50] J. F. Stanton, J. Gauss, and O. Christiansen, J. Chem. Phys. **114**, 2993 (2001).
[51] J. M. Rintelman and M. S. Gordon, J. Chem. Phys. **115**, 1795 (2001).
[52] K. W. Sattelmeyer, H. F. Schaefer III, and J. F. Stanton, J. Chem. Phys. **116**, 9151 (2002).

Downloaded 31 Jan 2003 to 141.52.232.84. Redistribution subject to AIP license or copyright, see http://ojps.aip.org/jcpo/jcpcr.jsp