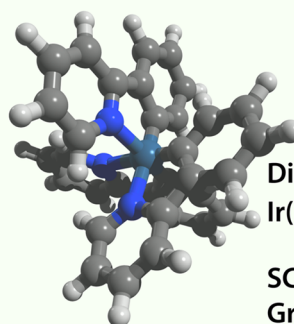


Analytical Nuclear Gradients of Density-Fitted Dirac–Fock Theory with a 2-Spinor Basis

Toru Shiozaki*

Department of Chemistry, Northwestern University, 2145 Sheridan Rd., Evanston, Illinois 60208, United States

ABSTRACT: An efficient algorithm is presented for evaluating the analytical nuclear gradients of density-fitted four-component relativistic Dirac–Fock theory as an initial step toward realizing large-scale geometry optimization of heavy-element complexes. Our algorithm employs kinetically balanced 2-spinor basis functions for the small components. The computational cost of nuclear gradient evaluation is found to be smaller than that of a Dirac–Fock self-consistent iteration. Timing data are presented for $\text{Ir}(\text{ppy})_3$ (61 atoms) using a double- ζ basis set.



Dirac–Fock @ 1024 cores
 $\text{Ir}(\text{ppy})_3$, DZ, nosym

SCF (1 iter.) 113 sec.
Gradients 58 sec.

Since the analytical procedure to compute nuclear gradients was invented in the late 1960s,¹ geometry optimization has become routine work in quantum chemical applications, allowing us to obtain equilibrium geometries and transition states of molecular systems.² Optimized geometries are the basis for calculating molecular properties such as spectroscopic and thermodynamic constants. Efficient analytical gradient algorithms have been formulated in the nonrelativistic framework for the Hartree–Fock, Kohn–Sham, complete-active-space self-consistent field (CASSCF), and various electron correlation methods (see ref 3 and references therein). Especially those using density fitting have enabled geometry optimization of 100-atom systems or larger.^{4–14} In contrast, in the relativistic framework for heavy-element complexes,^{15–21} analytical gradient techniques have not been well explored. This is partly because relativistic electronic structure theories were not applicable to large systems until very recently,^{22,23} for which analytical computation of nuclear gradients is more advantageous than numerical differentiation.

However, the recent development of theories, algorithms, and parallel computer programs has enabled fully relativistic four-component computations of electronic structures of large heavy-element complexes. In particular, the author has developed an efficient Dirac–Fock algorithm using density fitting and 2-spinor basis functions and demonstrated that Dirac–Fock calculations for a 100-atom system with a few heavy elements can be performed routinely.²³ For instance, a Dirac–Fock self-consistent iteration for a 130-atom molecule with an actinide atom took only 1100 s on an in-house computer cluster (1024 CPU cores). The computational cost was found to be 70–90 times that of a closed-shell nonrelativistic Hartree–Fock iteration. In addition, the density fitting approximation in the relativistic framework has been shown to be as accurate as the nonrelativistic density fitting.²³ The proposed algorithm is closely related to the pseudospectral

approach by Nakajima and Hirao²⁴ and the density-fitted density functional algorithm of Belpassi and co-workers.^{17,25,26} Very recently, Baldes and Weigend have reported an efficient gradient implementation of two-component effective core potential methods.²⁷ With this in mind, it is now of great importance to develop efficient nuclear gradient theory on the basis of the four-component Dirac approaches.

Most of the previous studies on analytical nuclear gradients in the relativistic framework were focused on approximate scalar or two-component methods.^{16,20,28} They include that of a quasi-relativistic framework,²⁹ the Douglas–Kroll–Hess approach,^{30–32} the direct perturbation theory,^{33–35} the zeroth-order regular approximation,^{36–38} the normalized elimination of the small component approximation,^{39–41} and the relativistic elimination of small components approximation.⁴² Cheng and Gauss have studied a nuclear derivative algorithm for spin-free exact two-component theories.⁴³ There have been a few implementations of analytical nuclear gradients of fully relativistic Dirac–Fock and Dirac–Kohn–Sham theories,^{44,45} albeit limited to few-atom systems.

In this letter, we present an efficient algorithm for computing analytical gradients of the density-fitted Dirac–Fock method. This work can be seen as a first step toward establishing theories and algorithms for geometry optimization of sizable heavy-element complexes. The algorithm is an extension of the Dirac–Fock algorithm reported for energy evaluations by us²³ and utilizes the intermediate factorization for computational efficiency. The working equations have been implemented into a parallel code using a similar abstraction of the equations to those reported in the previous work (see below).²³ This work is also applicable to single-state CASSCF with straightforward

Received: August 12, 2013

modifications, if CASSCF orbitals and two-particle density matrices are provided, and will be the basis for analytical gradient algorithms of multistate CASSCF and electron correlation methods.

Unless otherwise stated, the following index notation is used: r, s, t , and u label atomic basis functions (or atomic orbitals, AO); i and j label occupied molecular orbitals (MO); γ and δ are indices for auxiliary basis functions; and X, Y, Z , and W denote large components (L^\pm) or small components (S^\pm). The many-electron Dirac Hamiltonian is

$$\hat{H} = \sum_i [c^2(\beta - I_4) + c(\alpha \cdot \hat{\mathbf{p}}) + \hat{V}_i^{\text{nuc}}] + \sum_{i < j} \hat{g}(i, j) \quad (1)$$

where c is the speed of light, $\hat{\mathbf{p}}$ is the momentum operator, \hat{V}^{nuc} is the nuclear attraction operator, I_4 is the unit matrix, and β and α are the Dirac matrices. In this work, we use the Dirac–Coulomb Hamiltonian [i.e., $\hat{g}(1, 2) = 1/r_{12}$], which ignores the spin–spin and spin–other-orbit interactions and the retardation effects of the electron–electron interaction. We note that Dirac–Fock algorithms with the so-called Gaunt or Breit interactions have also been developed in our previous study,^{23,46} and analytical gradient theory based on these interactions will be considered in the future. The following is based on the assumption that a variational procedure using this many-electron Dirac Hamiltonian provides an accurate approximation to the exact solution in quantum electrodynamics. See discussions on the so-called Brown–Ravenhall disease in ref 20. Similarly to the approaches by Quiney et al.^{47,48} and by Yanai et al.,^{49–51} we use a 2-spinor basis that satisfies the so-called kinetic balance, that is,

$$\Phi_r^{S^\pm} = \frac{\alpha \cdot \hat{\mathbf{p}}}{2c} \Phi_r^{L^\pm} \quad (2)$$

with $\Phi_r^{L^+} = (\phi_r^l, 0, 0, 0)^T$ and $\Phi_r^{L^-} = (0, \phi_r^l, 0, 0)^T$. Here, we introduce a shorthand notation for AOs and their derivative with respect to the Cartesian coordinates:

$$\phi_r^w(\mathbf{r}) = \begin{cases} \phi_r(\mathbf{r}) & w = l \\ \frac{\partial \phi_r(\mathbf{r})}{\partial w} & w = x, y, z \end{cases} \quad (3)$$

Also, we define the two-electron Coulomb integrals over these basis functions:

$$(\chi_\gamma | \phi_r^w \phi_s^{w'}) = \iint \chi_\gamma(\mathbf{r}_1) \frac{1}{r_{12}} \phi_r^w(\mathbf{r}_2) \phi_s^{w'}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (4)$$

$$(\mathcal{J})_{\gamma\delta} = \iint \chi_\gamma(\mathbf{r}_1) \frac{1}{r_{12}} \chi_\delta(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (5)$$

for later convenience. The density-fitted Dirac–Fock energy can be computed using the above integrals as

$$E_{\text{DF}} = \sum_{XY} \sum_{rs} D_{sr}^{YX} h_{rs}^{XY} + \frac{1}{2} \sum_{XYZW} \sum_{rstu} (D_{sr}^{YX} D_{tu}^{WZ} - D_{st}^{YZ} D_{ur}^{WX}) \sum_{\gamma\delta} (\Phi_r^{X\dagger} \Phi_s^Y | \chi_\gamma) (\mathcal{J}^{-1})_{\gamma\delta} (\chi_\delta | \Phi_t^{Z\dagger} \Phi_u^W) \quad (6)$$

in which D_{tu}^{XY} is a density matrix element defined as $D_{tu}^{XY} = \sum_i C_{ti}^X C_{ui}^{Y*}$ (C_{ti}^X is a molecular coefficient of component X), and

$$(\chi_\gamma | \Phi_r^{X\dagger} \Phi_u^Y) = \sum_{w,w' \in \{l,x,y,z\}} (\chi_\gamma | \phi_r^w \phi_u^{w'}) k_{ww'}^{XY} \quad (7)$$

The component-dependent factor $k_{ww'}^{XY}$ is computed using a compact formula:

$$k_{ww'}^{XY} = v^{X\dagger} \eta_w^\dagger \eta_{w'}^Y v^Y \quad (8)$$

where $v^X = (\delta_{X,L^+}, \delta_{X,L^-}, \delta_{X,S^+}, \delta_{X,S^-})^T$ and

$$\eta_w = \begin{cases} \begin{pmatrix} I_2 & 0_2 \\ 0_2 & 0_2 \end{pmatrix} & w = l \\ -\frac{i}{2c} \begin{pmatrix} 0_2 & 0_2 \\ 0_2 & \sigma_w \end{pmatrix} & w = x, y, z \end{cases} \quad (9)$$

with 0_2 , I_2 , and σ being the two-by-two zero, identity, and Pauli matrices, respectively. The Dirac–Fock equation can be derived by taking derivatives of E_{DF} [eq 6] with respect to C^{X*} .

The working equations for evaluating the Coulomb and exchange matrices are

$$(\mathbf{J}^{XY})_{rs} = \sum_\gamma (\Phi_r^{X\dagger} \Phi_s^Y | \chi_\gamma) C_\gamma \quad (10)$$

$$(\mathbf{K}^{XY})_{rs} = \sum_\gamma \sum_i (\Phi_r^{X\dagger} \bar{\Psi}_i | \tilde{\chi}_\gamma) (\tilde{\chi}_\gamma | \bar{\Psi}_i^\dagger \Phi_s^Y) \quad (11)$$

in which we used the following intermediates:

$$C_\gamma = \sum_\delta (\mathcal{J}^{-1/2})_{\gamma\delta} \mathcal{D}_\delta \quad (12)$$

$$\mathcal{D}_\gamma = \sum_X \sum_{i,r} (\Phi_r^{X\dagger} \bar{\Psi}_i | \tilde{\chi}_\gamma) C_{ri}^{X*} \quad (13)$$

$$(\Phi_r^{X\dagger} \bar{\Psi}_i | \tilde{\chi}_\gamma) = \sum_\delta (\mathcal{J}^{-1/2})_{\gamma\delta} \left[\sum_W (\Phi_r^{X\dagger} \Psi_i^W | \chi_\delta) \right] \quad (14)$$

$$(\Phi_r^{X\dagger} \Psi_i^W | \chi_\gamma) = \sum_{w,w' \in \{l,x,y,z\}} k_{ww'}^{XW} \left[\sum_s (\phi_r^w \phi_s^{w'} | \chi_\gamma) C_{si}^W \right] \quad (15)$$

C_γ and \mathcal{D}_γ are real in Dirac–Coulomb–Fock calculations due to symmetry. As we have shown,²³ the factorization of the three-index intermediates in eq 14 is the key to arriving at an efficient algorithm.

The simplest way to derive nuclear gradient formulas is to use a Lagrangian that takes into account orbital orthogonality:

$$L = E_{\text{DF}} - \text{Tr}[\mathbf{X}(\mathbf{C}^\dagger \mathbf{S} \mathbf{C} - \mathbf{1})] \quad (16)$$

where \mathbf{C} and \mathbf{S} are four-component coefficient and overlap matrices, and \mathbf{X} is a Lagrange multiplier. By taking the derivative with respect to \mathbf{C}^\dagger , one can show that the nonzero elements of \mathbf{X} are $X_{ij} = \delta_{ij} \varepsilon_i$ with i being an occupied orbital (ε_i is its orbital energy).¹ The one-electron contribution to the nuclear gradients is

$$L_1^{\mathbf{q}} = \text{Tr}[\mathbf{D} \mathbf{h}^{\mathbf{q}} - \mathbf{W} \mathbf{S}^{\mathbf{q}}] \quad (17)$$

in which $\mathbf{W} = \mathbf{C} \mathbf{X} \mathbf{C}^\dagger$ and \mathbf{q} denotes any nuclear displacements. The explicit formula in terms of derivative AO integrals is

$$\begin{aligned}
L_1^{\mathbf{q}} = & \sum_{rs} [\mathcal{R}(D_{rs}^{L^+L^+} + D_{rs}^{L^-L^-})V_{rs}^{\text{nuc},\mathbf{q}} \\
& + \sum_{X,Y \in \{S^+,S^-\}} \mathcal{R}(k_{ww}^{XY}D_{sr}^{YX})V_{rs}^{\text{nuc},ww',\mathbf{q}} + \mathcal{R}(2D_{rs}^{S^+L^+} \\
& + 2D_{rs}^{S^-L^-} - D_{rs}^{S^+S^+} - D_{rs}^{S^-S^-} - \frac{1}{2c^2}W_{rs}^{S^+S^+} \\
& - \frac{1}{2c^2}W_{rs}^{S^-S^-})T_{rs}^{\mathbf{q}} - \mathcal{R}(W_{rs}^{L^+L^+} + W_{rs}^{L^-L^-})S_{rs}^{\mathbf{q}}] \quad (18)
\end{aligned}$$

where $V_{rs}^{\text{nuc},\mathbf{q}}$, $T_{rs}^{\mathbf{q}}$, and $S_{rs}^{\mathbf{q}}$ are the derivatives of the nuclear attraction potential, kinetic operator, and overlap integrals, respectively. Due to symmetry, only the real part of the density matrices contributes to the gradients.

For the two-electron contribution, it is convenient to introduce three- and two-index effective density matrices:

$$\Gamma_{\gamma,rs}^{ww'} = \sum_{XY} k_{ww'}^{XY*} [C_{\gamma}D_{rs}^{XY} - \sum_{ij} (\check{\chi}_{\gamma}|\bar{\Psi}_i^{\dagger}\bar{\Psi}_j)C_{ri}^XC_{sj}^{Y*}] \quad (19)$$

$$\Gamma_{\gamma\delta} = C_{\gamma}C_{\delta} - \sum_{ij} (\check{\chi}_{\gamma}|\bar{\Psi}_i^{\dagger}\bar{\Psi}_j)(\bar{\Psi}_j^{\dagger}\bar{\Psi}_i|\check{\chi}_{\delta}) \quad (20)$$

using the fully transformed MO integrals

$$(\check{\chi}_{\gamma}|\bar{\Psi}_i^{\dagger}\bar{\Psi}_j) = \sum_{\delta} (\mathcal{J}^{-1/2})_{\gamma\delta}(\tilde{\chi}_{\delta}|\bar{\Psi}_i^{\dagger}\bar{\Psi}_j) \quad (21)$$

$$(\tilde{\chi}_{\delta}|\bar{\Psi}_i^{\dagger}\bar{\Psi}_j) = \sum_Y \sum_s (\tilde{\chi}_{\delta}|\bar{\Psi}_i^{\dagger}\Phi_s^Y)C_{sj}^Y \quad (22)$$

C_{δ} and $(\tilde{\chi}_{\delta}|\bar{\Psi}_i^{\dagger}\Phi_s^Y)$ may be available from preceding energy calculations. It is important to express the density matrices in terms of three-index MO integrals that are independent of component X for computational efficiency [especially for back transformation to three-index AO integrals in eq 19]. Using these density matrices, the two-electron contribution to the nuclear gradients can be simply written as

$$L_2^{\mathbf{q}} = \sum_{ww'} \sum_{rs} \sum_{\gamma} \mathcal{R}(\Gamma_{\gamma,rs}^{ww'}) (\chi_{\gamma}|\phi_r^w\phi_s^{w'})^{\mathbf{q}} - \frac{1}{2} \sum_{\gamma\delta} \mathcal{R}(\Gamma_{\gamma\delta}) \mathcal{J}_{\gamma\delta}^{\mathbf{q}} \quad (23)$$

Note again that we only need the real part of the density matrices, which reduces the computational cost of the second back transformation in eq 19.

In our implementation, the small-component three-index Coulomb integrals are computed by inserting the exact resolution of the identity (RI) as

$$(\chi_{\gamma}|\phi_r^w\phi_s^{w'}) = \sum_{r' \leftarrow r} \sum_{s' \leftarrow s} (\chi_{\gamma}|\bar{\phi}_{r'}\bar{\phi}_{s'})\mathcal{M}_{r'r}^w\mathcal{M}_{s's'}^{w'} \quad (24)$$

$$\mathcal{M}^w = \mathcal{S}^{-1}\mathcal{P}^w \quad (25)$$

$$\mathcal{P}_{rs}^w = \int \bar{\phi}_r(\mathbf{r})\phi_s^w(\mathbf{r})\mathrm{d}\mathbf{r} \quad (26)$$

$$S_{rs} = \int \bar{\phi}_r(\mathbf{r})\bar{\phi}_s(\mathbf{r})\mathrm{d}\mathbf{r} \quad (27)$$

where $\bar{\phi}_r$ is a Cartesian Gaussian function in which $\nabla\phi_r$ can be exactly expanded. It is worth noting that \mathcal{M} , \mathcal{P} , and \mathcal{S} are localized to each shell of basis functions and not global matrices. The derivatives of the three-index integrals with respect to nuclear displacements are then expressed as

$$(\chi_{\gamma}|\phi_r^w\phi_s^{w'})^{\mathbf{q}} = \sum_{r's'} (\chi_{\gamma}|\bar{\phi}_{r'}\bar{\phi}_{s'})^{\mathbf{q}}\mathcal{M}_{r'r}^w\mathcal{M}_{s's'}^{w'} \quad (28)$$

which follows from $\mathcal{M}_{rs}^{w,\mathbf{q}} = 0$ (because \mathcal{M}_{rs}^w is a one-center integral). In our program, \mathcal{M}_{rs} is precomputed and stored in a basis shell object. Note that this formula implies that evaluation of higher-order derivative integrals is also trivial. The contraction of the 3-index density matrices to the gradient integrals is performed in practice as

$$\begin{aligned}
& \sum_{ww'} \sum_{rs} \sum_{\gamma} \mathcal{R}(\Gamma_{\gamma,rs}^{ww'}) (\chi_{\gamma}|\phi_r^w\phi_s^{w'})^{\mathbf{q}} \\
& = \sum_{r's' \leftarrow rs} \sum_{\gamma} (\chi_{\gamma}|\bar{\phi}_{r'}\bar{\phi}_{s'})^{\mathbf{q}} [\sum_{ww'} \sum_{rs} \mathcal{R}(\Gamma_{\gamma,rs}^{ww'})\mathcal{M}_{r'r}^w\mathcal{M}_{s's'}^{w'}] \quad (29)
\end{aligned}$$

in which the transformation in the square bracket is localized to each basis shell. Finally, the total nuclear gradients are calculated as $L^{\mathbf{q}} = L_1^{\mathbf{q}} + L_2^{\mathbf{q}}$.

To demonstrate the efficiency of our algorithm, the timing data for Ir(pppy)₃ [fac-tris(2-phenylpyridine)iridium] are shown in Table 1. We used the def2-SVP basis set⁵² except for Ir, for

Table 1. Wall Times in Seconds for Computing Nuclear Gradients of Ir(pppy)₃ (61 Atoms, 699 Basis Functions) Using the Hartree–Fock and Dirac–Fock Methods^a

step	Hartree–Fock	Dirac–Fock	equation
SCF (1 iter.)	1.7	113.5	
gradients	5.2	57.7	
one-body densities	0.1	1.2	18
second transform	0.2	15.9	21, 22
2-index density	0.4	1.9	20
first back transform	0.0	2.1	19
second back transform	0.3	10.8	19
integral contraction	4.1	25.8	

^aA computer cluster of 128 Xeon E5-2650 2.00 GHz (1024 cores) was used.

which a subset of the ANO-RCC basis set⁵³ [8s7p5d3f] was used. The fitting functions were constructed from a union of the def2-SVP-JKFIT⁵⁴ and uncontracted ANO-RCC basis sets. The numbers of the orbital and auxiliary basis functions were 699 and 3435, respectively. All of the computations were performed on a computer cluster of a 2.00 GHz 128 Xeon E5-2650 (1024 cores) using the BAGEL package.⁵⁵ Our relativistic code in BAGEL does not take advantage of spacial or time reversal symmetry so far. As shown in Table 1, the evaluation of the nuclear gradients was found to be *cheaper* than a Dirac–Fock self-consistent iteration (including the diagonalization step). This is because one can multiply fully transformed MO integrals and $\mathcal{J}^{-1/2}$ in the gradient algorithm [eq 21]. A total geometry optimization step took typically 30–50 min. The parallel efficiency (the strong scaling between 512 and 1024 cores) has been 59% and 62% for Dirac–Fock SCF and gradient computations, respectively. This encouraging result, together with the efficient SCF algorithm,²³ warrants further development of analytic gradient theory of fully relativistic approaches for large heavy-element complexes, such as (multistate) CASSCF, electron correlation methods, and density functional theory.

To conclude, we have developed an efficient algorithm for evaluating the analytical nuclear gradients of a large heavy-

element complex using the density-fitted four-component Dirac–Fock method. The key results are the expressions for effective density matrices in terms of factorized three-index MO integrals [eqs 19 and 20], which lead to an economical procedure for back transformation to AO integrals that are to be contracted with the gradient integrals. In addition, the shell-wise contraction at the uncontracted level [eq 29] takes advantage of compact 2-spinor basis functions. The proposed algorithm has been implemented into an efficient parallel code in the BAGEL package, which is openly available under the GNU General Public License.⁵⁵

AUTHOR INFORMATION

Corresponding Author

*E-mail: shiozaki@northwestern.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work has been supported by the Initiative for Sustainability and Energy at Northwestern (ISEN) Booster Award.

REFERENCES

- (1) Pulay, P. *Mol. Phys.* **1969**, *17*, 197–204.
- (2) Schlegel, H. B. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2011**, *1*, 790–809.
- (3) Pulay, P. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; Vol. 2, Chapter 19, pp 1191–1240.
- (4) Weigend, F.; Häser, M. *Theor. Chem. Acc.* **1997**, *97*, 331–340.
- (5) Hättig, C. *J. Chem. Phys.* **2003**, *118*, 7751–7761.
- (6) Köhn, A.; Hättig, C. *J. Chem. Phys.* **2003**, *119*, 5021–5036.
- (7) Rhee, Y. M.; DiStasio, R. A.; Lochan, R. C.; Head-Gordon, M. *Chem. Phys. Lett.* **2006**, *426*, 197–203.
- (8) Neese, F.; Schwabe, T.; Grimme, S. *J. Chem. Phys.* **2007**, *126*, 124115.
- (9) Armbruster, M. K.; Weigend, F.; van Wüllen, C.; Klopper, W. M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 1748–1756.
- (10) Rhee, Y. M.; Casanova, D.; Head-Gordon, M. *J. Chem. Theory Comput.* **2009**, *5*, 1224–1236.
- (11) Loibl, S.; Manby, F. R.; Schütz, M. *Mol. Phys.* **2010**, *108*, 477–485.
- (12) Plessow, P.; Weigend, F. *J. Comput. Chem.* **2012**, *33*, 810–816.
- (13) Boström, J.; Aquilante, F.; Pedersen, T. B.; Lindh, R. *J. Chem. Theory Comput.* **2013**, *9*, 204–212.
- (14) Györfy, W.; Shiozaki, T.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2013**, *138*, 104104.
- (15) Visscher, L. *J. Comput. Chem.* **2002**, *23*, 759–766.
- (16) Saue, T. *ChemPhysChem* **2011**, *12*, 3077–3094.
- (17) Belpassi, L.; Storch, L.; Quiney, H. M.; Tarantelli, F. *Phys. Chem. Chem. Phys.* **2011**, *13*, 12368–12394.
- (18) Liu, W. *Phys. Chem. Chem. Phys.* **2012**, *14*, 35–48.
- (19) Fleig, T. *Chem. Phys.* **2012**, *395*, 2–15.
- (20) Kutzelnigg, W. *Chem. Phys.* **2012**, *395*, 16–34.
- (21) Liu, W.; Lindgren, I. *J. Chem. Phys.* **2013**, *139*, 014108.
- (22) Peng, D.; Middendorf, N.; Weigend, F.; Reiher, M. *J. Chem. Phys.* **2013**, *138*, 184105.
- (23) Kelley, M. S.; Shiozaki, T. *J. Chem. Phys.* **2013**, *138*, 204113.
- (24) Nakajima, T.; Hirao, K. *J. Chem. Phys.* **2004**, *121*, 3438–3445.
- (25) Belpassi, L.; Tarantelli, F.; Sgamellotti, A.; Quiney, H. M. *J. Chem. Phys.* **2006**, *124*, 124104.
- (26) Storch, L.; Belpassi, L.; Tarantelli, F.; Sgamellotti, A.; Quiney, H. M. *J. Chem. Theory Comput.* **2010**, *6*, 384–394.
- (27) Baldes, A.; Weigend, F. *Mol. Phys.* **2013**, DOI: 10.1080/00268976.2013.802037.
- (28) Nakajima, T.; Hirao, K. *Chem. Rev.* **2012**, *112*, 385–402.
- (29) Schreckenback, G.; Ziegler, T.; Li, J. *Int. J. Quantum Chem.* **1995**, *56*, 477–488.
- (30) Nasluzov, V. A.; Rösch, N. *Chem. Phys.* **1996**, *210*, 413–425.
- (31) Matveev, A. V.; Nasluzov, V. A.; Rösch, N. *Int. J. Quantum Chem.* **2007**, *107*, 3236–3249.
- (32) de Jong, W. A.; Harrison, R. J.; Dixon, D. A. *J. Chem. Phys.* **2001**, *114*, 48–53.
- (33) van Wüllen, C. *J. Chem. Phys.* **1996**, *105*, 5485–5493.
- (34) van Wüllen, C. *J. Chem. Phys.* **1998**, *109*, 392–399.
- (35) van Wüllen, C. *J. Comput. Chem.* **1999**, *20*, 51–62.
- (36) van Lenthe, E.; Ehlers, A.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943–8953.
- (37) van Lenthe, J. H.; Faas, S.; Snijders, J. G. *Chem. Phys. Lett.* **2000**, *328*, 107–112.
- (38) van Lenthe, J. H.; Van Ling, J. N. *Int. J. Quantum Chem.* **2006**, *106*, 2525–2528.
- (39) Filatov, M.; Cremer, D. *Chem. Phys. Lett.* **2003**, *370*, 647–653.
- (40) Filatov, M.; Cremer, D. *J. Chem. Phys.* **2003**, *118*, 6741–6750.
- (41) Zou, W.; Filatov, M.; Cremer, D. *J. Chem. Phys.* **2011**, *134*, 244117.
- (42) Fedorov, D. G.; Nakajima, T.; Hirao, K. *Chem. Phys. Lett.* **2001**, *335*, 183–187.
- (43) Cheng, L.; Gauss, J. *J. Chem. Phys.* **2012**, *135*, 084114.
- (44) Wang, F.; Li, L. *J. Comput. Chem.* **2002**, *23*, 920–927.
- (45) Varga, S.; Rosén, A.; Sepp, W.-D.; Fricke, B. *Phys. Rev. A* **2001**, *63*, 022510.
- (46) Shiozaki, T. *J. Chem. Phys.* **2013**, *138*, 111101.
- (47) Quiney, H. M.; Skaane, H.; Grant, I. P. *Adv. Quantum Chem.* **1998**, *32*, 1–49.
- (48) Grant, I. P.; Quiney, H. M. *Int. J. Quantum Chem.* **2000**, *80*, 283–297.
- (49) Yanai, T.; Nakajima, T.; Ishikawa, Y.; Hirao, K. *J. Chem. Phys.* **2001**, *114*, 6526–6538.
- (50) Yanai, T.; Nakajima, T.; Ishikawa, Y.; Hirao, K. *J. Chem. Phys.* **2002**, *116*, 10122.
- (51) Yanai, T.; Nakano, H.; Nakajima, T.; Tsuneda, T.; Hirata, S.; Kawashima, Y.; Nakao, Y.; Kamiya, M.; Sekino, H.; Hirao, K. *UTChem – A program for ab initio quantum chemistry*, Computational Science – ICCS: Berlin, Germany, 2003; Elsevier: New York, 2003; pp 84–95.
- (52) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571–2577.
- (53) Roos, O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2005**, *109*, 6575–6579.
- (54) Weigend, F. *J. Comput. Chem.* **2007**, *29*, 167–175.
- (55) BAGEL, Brilliantly Advanced General Electronic-structure Library. <http://www.nubakery.org> under the GNU General Public License (accessed on Sept. 11, 2013).