

## Dual-Basis Analytic Gradients. 1. Self-Consistent Field Theory

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Analytic gradients of dual-basis Hartree-Fock and density functional theory energies have been derived and implemented, which provide the opportunity for capturing large basis-set gradient effects at reduced cost. Suggested pairings for gradient calculations are 6-31G/6-31G\*\*, dual[-f,-d]/cc-pVTZ, and 6-311G\*/6-311++G(3df,3pd). Equilibrium geometries are produced within 0.0005 Å of large-basis results for the latter two pairings. Though a single, iterative SCF response equation must be solved (unlike standard SCF gradients), it may be obtained in the smaller basis set, and integral screening further reduces the cost for well-chosen subsets. Total nuclear force calculations exhibit up to 75% savings, relative to large-basis calculations.

### Introduction

The derivation and implementation of analytic energy gradients<sup>1–9</sup> have been a fundamental driving force for the usefulness of computational quantum chemistry. Nuclear forces, in particular, allow for the efficient optimization of molecular geometries and transition states,<sup>10–13</sup> intrinsic reaction coordinates,<sup>14–16</sup> and, more recently, *ab initio* molecular dynamics (AIMD).<sup>17–20</sup> Density functional theory (DFT) has essentially replaced Hartree-Fock (HF) as a stand-alone method for both single-reference energies and gradients, due to its comparable cost and scaling while including parametrized electron correlation; however, HF is still often used as the reference energy for subsequent perturbative correlation calculations.

Although much effort<sup>22–31</sup> has been made to reduce the cost of self-consistent field (SCF) energy calculations (encompassing both DFT and HF) with respect to system size, little progress has been made on the basis set front. Large basis sets and tight numerical thresholds produce results that are both stable and reliable, the kind of results required for accurate energetics and quantitative computational chemistry. Unfortunately, this regime of high precision and accuracy is inherently unsuited to many of the linear scaling techniques cited above. Extended basis sets, for example, necessarily reduce the natural sparsity in the overlap matrix, the inverse of which is needed in most linear scaling algorithms. Thus, although the formal  $N^4$  scaling (where  $N$  is the total number of atomic basis functions) has been reduced to roughly order  $N$  with respect to system size for small basis sets and one-dimensional systems, higher system-size scalings are demonstrated for large basis sets, and the quartic scaling very nearly holds true with respect to basis set size. Additionally, large basis sets demonstrate the inherent errors of a given method only. Accidental error cancellations do occur (as is sometimes seen with small-basis HF molecular structures), but these are neither wholly systematic nor transferrable across systems. The commonly used B3LYP<sup>32,33</sup> functional, for

example, was parametrized at the complete basis limit, and errors ascribed to the functional itself are sometimes due to the pairing of a small basis set (6-31G, for example) with a large-basis-parametrized functional.<sup>34</sup>

Even linear scaling methods can prove intractable if the computational prefactor is high enough, and two current methods have shown noteworthy promise in this regard. Pseudospectral (PS) methods<sup>35–39</sup> replace the evaluation of the two-electron integrals with numerical evaluations on a molecular grid, and resolution of the identity (RI)/density fitting (DF)<sup>40–47</sup> methods expand the two-electron integrals in an atom-centered auxiliary basis. Both methods very successfully reduce the computational prefactor for small- to medium-sized molecules, and PS methods additionally reduce the basis set scaling (roughly  $N^3$ ). Numerical robustness of the PS method is sometimes lacking, however, leaving instabilities in potential energy surfaces and gradients. RI/DF methods lack this problem and have received considerable recent interest. Their system-size scaling is essentially unchanged, however, and thus leaves RI/DF unsuited to very large molecules (although linear-scaling DF algorithms are currently being pursued in our research group<sup>48</sup>). Although the method described in this paper follows a unique approach to SCF calculations, it is essentially stand-alone, and careful application of PS or RI/DF methods may provide future augmentations to our method for energy and analytic derivative calculations.

In general, SCF calculations are known to converge more quickly with respect to basis set size than correlated wave function methods.<sup>49–51</sup> However, heavily polarized quadruple- $\zeta$  up to even quintuple- $\zeta$  basis sets are still required to approach this convergence.<sup>49,51</sup> Molecular structures, on the other hand, are somewhat less sensitive to basis set effects,<sup>50</sup> or, at the very least, acceptable errors in structures translate to smaller errors in energies. Still, polarization functions beyond a minimal basis are typically required for even qualitatively correct structures, and polarized (and possibly augmented) triple- $\zeta$  or quadruple- $\zeta$  basis sets are required for quantitative convergence of structures.

The dual-basis method provides a means of perturbatively obtaining large-basis energies at roughly small-basis cost. After performing a fully converged SCF calculation in a small basis,

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a correction is formed from a single SCF step in the larger, target basis. Originally devised for HF, this method has also been applied to DFT<sup>52</sup> and MP2<sup>53–55</sup> energies. In both cases, large-basis bond energies are reproduced within roughly 0.02–0.05 kcal/mol, well below the inherent error for either method and several orders of magnitude smaller than the error due to using the smaller basis set alone. Here, we present the derivation and implementation of DB-SCF analytic gradients. Though the resulting theory requires the solution of a single SCF response equation,<sup>56</sup> we will show that the costly iterative portion may be solved in the small basis. This fact, combined with significant integral screening, provides useful savings for proper basis set pairings, in addition to the savings already inherent in the underlying DB-SCF energy calculation.

## 2. Methods

In the following section, the pertinent equations governing a dual-basis SCF gradient calculation are presented. We emphasize that we are constructing an exact first derivative of an approximate method; no approximations have been made to the gradient itself. The theory is presented in the unrestricted Kohn-Sham formalism; specializations to restricted calculations and Hartree-Fock are made when necessary. Repeated indices imply summation.

**2.1. Theory.** *2.1.1. Dual-Basis Energy.* A DB-SCF calculation<sup>52,53</sup> consists of a full SCF calculation in a small subset of the larger, target basis set; subsequently, the converged density matrix is projected into the large space and is followed by a single Roothaan (diagonalization) step. A correction, which accounts for first-order changes in the density matrix (or, alternatively, accounts for orbital relaxation) following this single SCF step, is then applied. The DB-SCF energy is expressed as

$$E_{\text{DB-SCF}} = E_{\text{small}} + \Delta E_{\text{DB}} \quad (1)$$

where  $E_{\text{small}}$  is the small-basis SCF energy in the atomic orbital (AO) basis

$$E_{\text{small}} = P_{\mu\nu}^{\text{tot}} H_{\mu\nu} + \frac{1}{2} P_{\mu\nu}^{\text{tot}} (\mu\nu|\lambda\sigma) P_{\lambda\sigma}^{\text{tot}} - \frac{\kappa}{2} P_{\mu\nu}^{\alpha} (\mu\lambda|\sigma\nu) P_{\lambda\sigma}^{\alpha} - \frac{\kappa}{2} P_{\mu\nu}^{\beta} (\mu\lambda|\sigma\nu) P_{\lambda\sigma}^{\beta} + E_{\text{xc}}(P^{\alpha}, P^{\beta}) \quad (2)$$

$H$  is the one-electron Hamiltonian,  $P$  is the density matrix resulting from the converged MO coefficients  $C$ ,  $\kappa$  is used as a scaling parameter of the HF exchange energy to include hybrid functionals ( $\kappa = 1$  for HF,  $\kappa = 0$  for “pure” functionals, and  $0 \leq \kappa \leq 1$  for hybrid functionals), and  $P^{\text{tot}} = P^{\alpha} + P^{\beta}$ . The exchange-correlation energy is represented by  $E_{\text{xc}}$ . Though this SCF energy is defined in the small basis, eq 2 is written in the large basis for notational simplicity. This change is permitted since, for proper subsets, the projection of the density matrix leaves new basis function terms unchanged.

The dual-basis energy correction is defined as

$$\Delta E_{\text{DB}} = (\Delta P)_{\mu\nu}^{\alpha} F_{\mu\nu}^{\alpha} + (\Delta P)_{\mu\nu}^{\beta} F_{\mu\nu}^{\beta} \quad (3)$$

where  $\Delta P = P' - P$  is the change in the density matrix upon diagonalization of  $F$ , where  $P'$  is the post-diagonalization density matrix. Here,  $F$  is the large-basis Fock matrix built from the converged small-basis density matrix

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu} + (\mu\nu|\lambda\sigma) P_{\lambda\sigma}^{\text{tot}} - \kappa (\mu\lambda|\sigma\nu) P_{\lambda\sigma}^{\alpha} + f_{\mu\nu}^{\alpha}(P^{\alpha}, P^{\beta}) \quad (4)$$

where  $f$  is the exchange-correlation contribution to the Fock matrix

$$f_{\mu\nu}^{\alpha} = \frac{\partial E_{\text{xc}}}{\partial P_{\mu\nu}^{\alpha}} \quad (5)$$

First, note that  $F$  is diagonalized by both the small-basis converged coefficients,  $C$ , as well as the large-basis post-diagonalization coefficients,  $C'$  (this fact only holds for proper subsets). Additionally, note that the exact  $E_{\text{xc}}$  is not constructed in the large basis, for this would require an additional  $E_{\text{xc}}$  build after diagonalization of the Fock matrix, as well as large-basis  $z$ -vector terms in the gradient. Instead, the exchange-correlation contribution to the dual-basis correction is  $\Delta P \cdot f$ ; the small-basis portion does not cancel.

*2.1.2. General Unrestricted Kohn-Sham Gradient and Response Theory.* The derivative of the small-basis energy with respect to nuclear coordinate  $x$  follows the standard form, where the superscript notation denotes a derivative and a parenthetical superscript denotes differentiation of AO quantities only

$$E_{\text{small}}^x = P_{\mu\nu} H_{\mu\nu}^x + \Gamma_{\mu\nu\lambda\sigma}^J (\mu\nu|\lambda\sigma)^x - \kappa \Gamma_{\mu\nu\lambda\sigma}^K (\mu\lambda|\sigma\nu)^x + W_{\mu\nu} S_{\mu\nu}^x + E_{\text{xc}}^{(x)} \quad (6)$$

where  $S$  is the AO overlap integral matrix. In eq 6, the common grouping of coefficient matrixes has been performed, resulting in one-particle ( $P$ ), two-particle ( $\Gamma$ ), and energy-weighted ( $W$ ) density matrices. Each is defined as follows:

$$P_{\mu\nu} = P_{\mu\nu}^{\text{tot}} \quad (7)$$

$$\Gamma_{\mu\nu\lambda\sigma}^J = \frac{1}{2} P_{\mu\nu}^{\text{tot}} \otimes P_{\lambda\sigma}^{\text{tot}} \quad (8)$$

$$\Gamma_{\mu\nu\lambda\sigma}^K = \frac{1}{2} P_{\mu\nu}^{\alpha} \otimes P_{\lambda\sigma}^{\alpha} + \frac{1}{2} P_{\mu\nu}^{\beta} \otimes P_{\lambda\sigma}^{\beta} \quad (9)$$

$$W_{\mu\nu} = -P_{\mu\lambda}^{\alpha} F_{\lambda\sigma}^{\alpha} P_{\sigma\nu}^{\alpha} - P_{\mu\lambda}^{\beta} F_{\lambda\sigma}^{\beta} P_{\sigma\nu}^{\beta} \quad (10)$$

An analytic nuclear derivative of the DB-HF energy, then, only requires the additional derivative of the dual-basis correction term. By our choice of the dual-basis energy correction (essentially a fixed-Hamiltonian formulation), derivatives with respect to orbital rotations in the large basis vanish. However, since the DB-SCF energy is not variationally optimized with respect to small basis orbital rotations, derivatives with respect to these parameters are nonzero. Solution of a single set of coupled-perturbed SCF (CP-SCF) equations (or  $z$ -vector equations<sup>56</sup>) is required; however, because of our choice of the DB energy correction, the iterative portion may be solved in the small basis.

Following the form of ref 57, the nuclear derivative of a molecular orbital coefficient is expressed as

$$C^x = C U^x \quad (11)$$

where  $U^x$  defines an orbital response matrix and  $C$  is treated as an  $x$ -independent constant on the right-hand side. Following the diagonalization of the large-basis Fock matrix, a new set of MO coefficients,  $C'$ , is obtained, producing the new density matrix,  $P'$ . Similarly, a derivative of these new coefficients is

$$(C')^x = (C') \tilde{U}^x \quad (12)$$

In other words, via the CP-SCF formulation, the goal is to find the first-order responses that leave the small-basis SCF converged.

With these tools in hand, the necessary derivatives are as follows. Here, we utilize a component notation for clarity, with the following conventions:

- $\mu, \nu, \lambda, \dots$  : all AOs
- $p, q, r, \dots$  : general MOs
- $i, j, k, \dots$  : occupied MOs
- $a, b, c, \dots$  : virtual MOs

Unless specified, all equations will be presented in the large basis set. Unadorned MO indices will represent matrices transformed by  $C$ , and primed MO indices will represent matrices transformed by  $C'$ . The Fock matrix  $F$  will always be the Fock matrix built from the (projected) small-basis density matrix,  $P$ .

The CP-SCF equations for the orbital responses are<sup>57</sup>

$$\bar{A}_{a\alpha i a b \alpha j a} U_{a\alpha i a}^x + \bar{A}_{a\beta i \beta b \alpha j a} U_{a\beta i \beta}^x = B_{b\alpha j a}^x \quad (13)$$

and an analogous  $\beta$  equation, obtained by interchange of  $\alpha \leftrightarrow \beta$ . The  $\bar{A}$  matrices are defined as

$$\bar{A}_{a\alpha i a b \alpha j a} = \delta_{a\alpha b a} \delta_{i\alpha j a} (\epsilon_{i\alpha} - \epsilon_{a\alpha}) + A_{a\alpha i a b \alpha j a} + f_{a\alpha i a, b\alpha j a} + f_{a\alpha i a, j\alpha b a} \quad (14)$$

where

$$A_{a\beta i \beta b \alpha j a} = A_{a\beta i \beta b \alpha j a} + f_{a\beta i \beta, b\alpha j a} + f_{a\beta i \beta, j\alpha b a} \quad (15)$$

where the implicit  $\alpha$  functional derivative of the  $\alpha$  exchange-correlation matrix,  $f^{\alpha, \alpha}$ , is defined as

$$f_{a\alpha i a, b\alpha k a} = \frac{\partial f_{a\alpha i a}(P^\alpha, P^\beta)}{\partial P_{b\alpha k a}} \quad (16)$$

The remaining matrices are

$$A_{a\alpha i a b \alpha j a} = 2(a^\alpha i^\alpha | b^\alpha j^\alpha) - \kappa(a^\alpha b^\alpha | i^\alpha j^\alpha) - \kappa(a^\alpha j^\alpha | i^\alpha b^\alpha) \quad (17)$$

$$A_{a\beta i \beta b \alpha j a} = 2(a^\beta i^\beta | b^\alpha j^\alpha) \quad (18)$$

$$B_{b\alpha j a}^x = F_{b\alpha j a}^{(x)} - S_{b\alpha j a}^{(x)} \epsilon_{j a} - \frac{1}{2} S_{i\alpha k a}^{(x)} A_{b\alpha j a i \alpha k a} - \frac{1}{2} S_{i\beta k \beta}^{(x)} A_{b\alpha j a i \beta k \beta} \quad (19)$$

where  $\epsilon$  denotes a molecular orbital energy. In the previous equations,  $F^{(x)}$  denotes a purely “skeleton” derivative (i.e., no derivatives of MO coefficients).

The  $z$ -vector method<sup>56</sup> reduces this set of  $3N$  equations (one for each nuclear perturbation) to one. For a given gradient expression, all terms multiplying *occ-virt* orbital response matrices define a Lagrangian,  $L$ , of the form  $L_{a^\alpha i^\alpha} U_{a\alpha i a}^x + L_{a^\beta i^\beta} U_{a\beta i \beta}^x$ . (Note that  $L^\alpha$  still may contain contribution from  $\beta$ -space quantities.) Subsequently, the  $x$ -independent  $z$ -vector is defined as

$$\bar{A}_{a\alpha i a b \alpha k a} z_{b\alpha k a} + \bar{A}_{a\alpha i a b \beta k \beta} z_{b\beta k \beta} = -L_{a\alpha i a} \quad (20)$$

with an analogous  $\beta$  equation. The  $z$ -vector is used to replace *occ-virt* responses as

$$L_{a\alpha i a} U_{a\alpha i a}^x + L_{a\beta i \beta} U_{a\beta i \beta}^x = z_{b\alpha k a} B_{b\alpha k a}^x + z_{b\beta k \beta} B_{b\beta k \beta}^x \quad (21)$$

Thus, by solving the single  $z$ -vector equation (20), all orbital

response terms may be replaced by  $z$  and the skeleton derivative matrices defining  $B^x$ .

**2.1.3. Dual-Basis Analytic Gradient.** The remaining task, therefore, is to determine the DB-SCF Lagrangian and substitute  $z$ -vector terms when necessary. In the following equations, only the  $\alpha$ -space terms will be shown. As usual, the concomitant  $\beta$ -space quantities may be obtained by interchange of  $\alpha \leftrightarrow \beta$ .

We may rewrite the DB energy correction as

$$Tr[(\Delta P)^\alpha F^\alpha] = \sum_i F_{i' a i' a}^\alpha - \sum_i F_{i a i a}^\alpha \quad (22)$$

The first required nuclear derivative is then

$$\begin{aligned} F_{i a i a}^x &= \frac{d}{dx} \left[ H_{i a i a} + \sum_k^{(\alpha)} [(i^\alpha i^\alpha | k^\alpha k^\alpha) - \kappa(i^\alpha k^\alpha | k^\alpha i^\alpha)] + \sum_k^{(\beta)} [(i^\alpha i^\alpha | k^\beta k^\beta)] + f_{i a i a}(P^\alpha, P^\beta) \right] \\ &= F_{i a i a}^{(x)} - \epsilon_{i a} S_{i a i a}^{(x)} - S_{j a k a}^{(x)} \left[ \frac{1}{2} A_{i a i a j a k a} + f_{i a i a, j a k a} \right] - \\ &\quad S_{j \beta k \beta}^{(x)} \left[ \frac{1}{2} A_{i a i a j \beta k \beta} + f_{i a i a, j \beta k \beta} \right] + U_{a k a}^x [A_{i a i a a k a} + f_{i a i a, a k a} + \\ &\quad f_{i a i a, k a a}] + U_{a \beta k \beta}^x [A_{i a i a a \beta k \beta} + f_{i a i a, a \beta k \beta} + f_{i a i a, k \beta a \beta}] \end{aligned} \quad (23)$$

where the identity,  $U_{pq}^x + U_{qp}^x + S_{pq}^{(x)} = 0$ , has been used.

In the subsequent derivative term, the fact that the Fock matrix is built from  $P$  allows for elimination of the large-basis responses

$$\begin{aligned} F_{i' a i' a}^x &= \frac{d}{dx} \left[ H_{i' a i' a} + \sum_k^{(\alpha)} [(i'^\alpha i'^\alpha | k^\alpha k^\alpha) - \kappa(i'^\alpha k^\alpha | k^\alpha i'^\alpha)] + \sum_k^{(\beta)} [(i'^\alpha i'^\alpha | k^\beta k^\beta)] + f_{i' a i' a}(P^\alpha, P^\beta) \right] \\ &= F_{i' a i' a}^{(x)} - 2\epsilon_{i' a} S_{i' a i' a}^{(x)} - S_{j a k a}^{(x)} \left[ \frac{1}{2} A_{i' a i' a j a k a} + f_{i' a i' a, j a k a} \right] - \\ &\quad S_{j \beta k \beta}^{(x)} \left[ \frac{1}{2} A_{i' a i' a j \beta k \beta} + f_{i' a i' a, j \beta k \beta} \right] + U_{a k a}^x [A_{i' a i' a a k a} + \\ &\quad f_{i' a i' a, a k a} + f_{i' a i' a, k a a}] + \\ &\quad U_{a \beta k \beta}^x [A_{i' a i' a a \beta k \beta} + f_{i' a i' a, a \beta k \beta} + f_{i' a i' a, k \beta a \beta}] \end{aligned} \quad (24)$$

where, in eq 24, we have used the fact that  $2\tilde{U}_{i' i'}^x = -1/2 S_{i' i'}^{(x)}$  and, thus, have eliminated all large-basis responses. In both cases, *occ-virt* response elements remain. Only response elements in the small basis are required, however, despite the fact that the Lagrangian contains contributions from large-basis functions

$$L_{a\alpha i a} = 2C_{\mu a \alpha} [(\mu \nu | \lambda \sigma) (\Delta P)_{\lambda \sigma}^{\text{tot}} - \kappa(\mu \lambda | \sigma \nu) (\Delta P)_{\lambda \sigma}^\alpha + f_{\mu \nu, \lambda \sigma}^{\alpha, \alpha} (\Delta P)_{\lambda \sigma}^\alpha + f_{\mu \nu, \lambda \sigma}^{\alpha, \beta} (\Delta P)_{\lambda \sigma}^\beta] C_{\nu i a} \quad (25)$$

In practice, the Lagrangian is actually implemented as  $1/2 L_{a i}$  and is later symmetrized so that its contribution to the AO-basis density matrix is formed as

$$(P_z)_{\mu \nu}^\alpha = \sum_{b k} C_{\mu b a} z_{b a k a} C_{\nu k a} + C_{\mu k a} z_{k a b a} C_{\nu b a} \quad (26)$$

With the Lagrangian in hand, the DB-SCF  $z$ -vector equation may be solved via eq 20. In using eq 20, note that the left-hand side may be constructed entirely in the small basis. The Fock-like right-hand side is constructed in the large basis (using additional dual-basis integral screening) and is projected back into the small basis prior to the transformation into the *occ-virt* space. Once the  $z$ -vector is obtained, the remaining gradient can be summarized in a conventional form

$$E_{\text{DB-SCF}}^x = \tilde{P}_{\mu\nu} H_{\mu\nu}^x + \tilde{\Gamma}_{\mu\nu\lambda\sigma}^J (\mu\nu|\lambda\sigma)^x - \kappa \tilde{\Gamma}_{\mu\nu\lambda\sigma}^K (\mu\lambda|\sigma\nu)^x + \tilde{W}_{\mu\nu} S_{\mu\nu}^x + E_{xc}^{(x)} + \tilde{X}_{\mu\nu} f_{\mu\nu}^{(x)} \quad (27)$$

where

$$\tilde{P}_{\mu\nu}^\alpha = P_{\mu\nu}^\alpha + (P_z)_{\mu\nu}^\alpha \quad (28)$$

$$(\tilde{\Gamma}^J)_{\mu\nu\lambda\sigma}^\alpha = \left( \tilde{P}_{\mu\nu}^\alpha - \frac{1}{2} P_{\mu\nu}^\alpha \right) \otimes P_{\lambda\sigma}^{\text{tot}} \quad (29)$$

$$(\tilde{\Gamma}^K)_{\mu\nu\lambda\sigma}^\alpha = \left( \tilde{P}_{\mu\nu}^\alpha - \frac{1}{2} P_{\mu\nu}^\alpha \right) \otimes P_{\lambda\sigma}^\alpha \quad (30)$$

$$\tilde{W}_{\mu\nu}^\alpha = -P_{\mu\lambda}^\alpha F_{\lambda\sigma}^\alpha P_{\sigma\nu}^\alpha - (P_z)_{\mu\lambda}^\alpha F_{\lambda\sigma}^\alpha P_{\sigma\nu}^\alpha - P_{\mu\gamma}^\alpha [(\gamma\delta|\lambda\sigma)(\tilde{P}_{\lambda\sigma}^{\text{tot}} - P_{\lambda\sigma}^{\text{tot}})] P_{\delta\nu}^\alpha - \kappa P_{\mu\gamma}^\alpha [(\gamma\lambda|\sigma\delta)(\tilde{P}_{\lambda\sigma}^\alpha - P_{\lambda\sigma}^\alpha)] P_{\delta\nu}^\alpha - P_{\mu\gamma}^\alpha [f_{\gamma\delta,\lambda\sigma}^{\alpha,\alpha} (\tilde{P}_{\lambda\sigma}^\alpha - P_{\lambda\sigma}^\alpha)] P_{\delta\nu}^\alpha - P_{\mu\gamma}^\alpha [f_{\gamma\delta,\lambda\sigma}^{\alpha,\beta} (\tilde{P}_{\lambda\sigma}^\beta - P_{\lambda\sigma}^\beta)] P_{\delta\nu}^\alpha \quad (31)$$

$$\tilde{X}_{\mu\nu}^\alpha = \tilde{P}_{\mu\nu}^\alpha - P_{\mu\nu}^\alpha \quad (32)$$

with analogous  $\beta$  terms so that  $\tilde{P}^{\text{tot}} = \tilde{P}^\alpha + \tilde{P}^\beta$ , for example. Specialization to closed-shell equations can be made by noting that  $\alpha$  and  $\beta$  matrices are identical, and specialization to DB-HF gradients can be made by letting  $\kappa = 1$  and  $E_{xc} = f_{xc} = 0$ .

**2.2. Algorithm and Assessment.** The schematic algorithm and cost assessment for a DB-HF gradient is described below. In assessing the cost,  $n$  refers to the number of small-basis functions, and  $N$  refers to the number of strictly large-basis functions. Unless otherwise specified, the scaling factors are presented with respect to basis set size.

**1. Small-Basis HF Calculation.** First, a full SCF calculation is performed in the small basis (cf. eq 2). The cost for this step scales as  $\mathcal{O}(C_n \times n^4/8)$ , where  $C_n$  is the number of small-basis HF steps required for convergence. The factor of 8 comes from the permutational symmetry of the electron repulsion integrals.

**2. Large-Basis DB-HF Correction.** A single Fock matrix is built in the large basis as  $F = H + IIP + f$ , where  $P$  is the projected density matrix produced from the small-basis SCF and  $I$  represents the full set of AO-basis electron repulsion integrals. This Fock build (normally an  $\mathcal{O}((n+N)^4/8)$  process) benefits from significant integral screening, as mentioned in ref 53. Integrals of the type  $(\mu\nu|\lambda\sigma)$  may be eliminated if  $\lambda$  or  $\sigma$  are strictly large-basis functions. Though the integrals are nonzero, their contraction with  $P_{\lambda\sigma}$  does not contribute to the energy for the new basis functions. Thus, the screening produces a scaling for the Fock build of

$$\mathcal{O}\left(\frac{3N^2n^2}{4} + \frac{Nn^3}{2} + \frac{n^4}{8}\right) \quad (33)$$

for simultaneous construction of Coulomb and exchange matrixes. For so-called “pure” functionals (in which only Coulomb contributions are required), the first term is reduced to  $N^2n^2/4$ .

This Fock matrix is then diagonalized to obtain new MO coefficients  $C'$  and a new density matrix  $P'$ . Note that the overall

savings factor (relative to an SCF calculation in the large basis) is

$$t_{\text{full}}^{\text{(dual)}} \approx \frac{\left[ \left( \frac{3N^2n^2}{4} + \frac{Nn^3}{2} + \frac{n^4}{8} \right) \times 1 \right] + \left[ \frac{n^4}{8} \times C_n \right]}{\frac{(n+N)^4}{8} \times C_N} \quad (34)$$

As a reference point, many of our truncations have  $n \approx N$ ; the target basis is roughly twice the size of the smaller basis set. For this truncation ratio and roughly 12 SCF cycles,  $t_{\text{full}}^{\text{(dual)}} \approx 0.12$ . The main savings stems from the single SCF step in the large basis but is tempered by the need for a full SCF calculation in the small basis. (Note that the above analysis must be augmented for system-size scaling, as sparsity and the number of significant shell pairs were excluded.)

Additionally, the exchange-correlation contribution has been neglected in eq 34 and is highly dependent on the choice of functional and quadrature grid. Though one more functional derivative appears in the dual-basis correction than in the DFT energy, this term is required at every step of a standard DFT calculation anyway during the construction of the Fock matrix. Existing DFT machinery can be used for implementation of this term, now built from  $P$  instead of  $P'$ . Note also that nearly all current functionals depend on spin densities ( $\rho^\alpha = P_{\mu\nu}^\alpha \phi_\mu \phi_\nu$ ) and, possibly, gradient invariants ( $\gamma^{\alpha\alpha} = P_{\mu\nu}^\alpha \nabla(\phi_\mu \phi_\nu)$ ). Standard techniques, therefore, designed to screen small values of  $P$  during the construction of  $f$ , will already inherently neglect large-basis density matrix terms and demonstrate savings in the exchange-correlation matrix construction.

With the new density and large-basis Fock matrix, the Dual-Basis correction  $\text{Tr}[\Delta P \cdot F]$  is calculated.

**3. Gradient.** Unlike standard SCF gradients, the  $z$ -vector equations (cf. eqs 20 and 25) must be solved for a DB-SCF gradient. However, integral screening and the fact that the iterative portion may be solved in the small basis make the cost tractable.

(a) The first step in the solution of the  $z$ -vector equations<sup>56</sup> is the construction of the Lagrangian, schematically represented as  $C_{\text{occ}}[(I + f^{\text{imp}})(P' - P)]C_{\text{virt}}$ , where  $f^{\text{imp}}$  signifies an implicit derivative of the XC matrix. Though the Fock-like term  $I(P' - P)$  must rigorously be formed in the large basis, the same screening that was exploited for the Fock build can also be used here because of the subsequent contraction with small-basis coefficients. This term is the secondary overall bottleneck in the gradient calculation. After construction and contraction of the integrals, the Fock-like matrix  $L$  is projected back into the small basis for use in the  $z$ -vector equations.

The DFT-specific portion of the Lagrangian requires work not present in a standard DFT calculation. One extra functional derivative (implicit derivative, in this case) is necessary, relative to a DFT gradient. Again, standard DFT routines can be utilized for this term, as long as the proper contracted density ( $P' - P$ ) is used.

(b) In the small basis, the iterative  $z$ -vector equations are solved. The cost  $[\mathcal{O}(C_z \times n^4/8)]$  is small, relative to the Lagrangian build for large basis set truncations. By transforming the MO-basis  $z$ -vector back to the AO basis, the  $z$ -vector's contribution to the 1PDM is obtained. At this stage, the DB-SCF relaxed dipole moment may be calculated.

(c) Most pieces of the energy-weighted density matrix (cf. eq 31) are now available. The  $z$ -vector equation gives  $I(P' - P)$  and  $f^{\text{imp}}(P' - P)$ . The remaining  $IIP_z$  and  $f^{\text{imp}}(P_z)$  can be



**TABLE 1: Errors in Dual-Basis DFT Geometries, Relative to Large (Target) Basis Set Geometries in Å<sup>a</sup>**

basis	single basis		dual basis			% recovery
	MAD	max	MAD	max	# above 0.01 Å	
6-31G/6-31G**	0.0391	0.188	0.0070	0.049	41	82.1
6-31G*/6-31++G**	0.0046	0.073	0.0003	0.009	0	93.5
6-311G/6-311++G(3df,3pd)	0.0446	0.217	0.0087	0.071	45	80.5
6-311G*/6-311++G(3df,3pd)	0.0083	0.050	0.0004	0.010	0	95.2
dual[-f,-inner d]/cc-pVTZ	0.0190 <sup>b</sup>	0.262 <sup>b</sup>	0.0005	0.005	0	97.4
dual[-f,-outer d]/cc-pVTZ			0.0014	0.011	1	92.6
dual[-f,-2d]/cc-pVTZ			0.0078	0.062	40	58.9

<sup>a</sup> MAD = mean absolute deviation; max = maximum absolute deviation. <sup>b</sup>cc-pVDZ was used as the small basis for comparison in these values.

formed in the small basis, at the cost of another  $\mathcal{O}(n^4/8)$  step. The contracted integrals can be read from disk, and the remainder of  $\tilde{W}$  is matrix multiplications.

(d) As in a normal SCF gradient, the most significant bottleneck is the construction and contraction of the derivative electron repulsion integrals with the 2PDM ( $\Gamma^{II^x}$ ). Most importantly, this term also benefits from the same type of integral screening discussed earlier. The “right” half of  $\tilde{\Gamma}$  in eqs 29 and 30 is  $P_{\lambda\sigma}$ , and thus, only integral derivatives  $(\mu\nu|\lambda\sigma)^x$  corresponding to small-small pairs of  $\lambda\sigma$  need to be calculated. This screening is implemented in the same fashion as in the Fock build and RHS integrals. Though the derivative ERIs formally scale as 9 times the cost shown in eq 33, the current implementation<sup>58</sup> in Q-Chem typically scales closer to 3 times the cost of a Fock build.

(e) The remaining DFT-only terms are  $E_{xc}^{(x)}$  and  $\tilde{X}_f^{(x)}$ . Although the former is a non-canceling term present in a standard DFT gradient, the latter term is somewhat akin to a term present only in the DFT Hessian. However, although the standard Hessian requires mixed terms of the form  $P^{xf^{(v)}}$  (and thus storage of the  $3N_{\text{atom}} \times N^2$  explicit derivative matrix), the DB-DFT gradient only requires the contraction with a single density,  $\tilde{X}_f^{(x)}$ , which can be folded into the functional derivative. At this time, this efficiency improvement has not been made to our code and represents a severe (but unnecessary) computational bottleneck. Thus, the timings presented in section 3.2 are demonstrated for DB-HF only.

Taking into account the significant computational bottlenecks, the relative cost factor produced by a DB-SCF gradient is

$$t_{\text{full}}^{\text{(dual)}} \approx \frac{3N^2n^2 + 2Nn^3 + (C_z + 5)\frac{n^4}{8} + t_{\text{dual}}^{xc}}{\frac{3(n+N)^4}{8} + t_{\text{large}}^{xc}} \quad (35)$$

where  $t^{xc}$  refers to the cost of exchange-correlation contributions in each basis set.

Note that, due to the loss of some permutational symmetry in the integrals, aggressive basis set truncations are required in order to demonstrate savings in the gradient alone. In the  $n \approx N$  regime, the gradient cost roughly breaks even ( $t \approx 1$ ) for DB-HF. For any nuclear force calculation, however, the underlying SCF calculation must be completed. The savings in this portion alone is enough to render the total force calculation faster. For example, assuming five z-vector iterations and 12 SCF iterations, eqs 34 and 35 can be combined to give a dual: full ratio of roughly 0.3 for  $n \approx N$ . In other words, an average DB-HF nuclear force calculation is roughly three times faster than the same job in the target basis.

**2.3. Basis Set Pairings.** Throughout the results provided in the next section, several common basis set pairings, denoted as small/target, are demonstrated. Previous tests of dual-basis

energies<sup>52,53</sup> have demonstrated that 6-311G\*\*<sup>59</sup> serves as a suitable subset for 6-311++G(3df,3pd),<sup>59–61</sup> the largest Pople-style optimized basis set available. We have also constructed the analogous subset for cc-pVTZ<sup>62,63</sup> by removing the set of  $f$  functions and the inner set of  $d$  functions on heavy atoms, leaving a  $4s3p1d$  subset for a  $4s3p2d1f$  target basis. The hydrogens have their set of  $d$  functions and the outer set of  $p$  functions eliminated, leaving a  $3s1p$  subset for a  $3s2p1d$  target basis. This pairing is denoted dual[-f,-d]/cc-pVTZ in the remainder of this paper. (Note that this truncation is slightly more aggressive than the truncation used for DB-MP2 energies in ref 53, where the T  $\rightarrow$  Q extrapolation of correlated energies was the goal.) Although cc-pVDZ<sup>62,63</sup> could also be used as a subset, only proper subsets have been explored in this work because of the savings due to integral screening at several stages of the calculation. We have not explored any of the augmented Dunning-type basis sets,<sup>64</sup> although preliminary tests suggest that aggressive truncation schemes are possible. These truncations will be the subject of future work on systems where diffuse functions are necessary. Although the dual-basis method is best suited for large basis sets, any improvements in the large molecule regime (for which small basis sets may be the only tractable option) would still be welcomed, as semiquantitative ab initio or DFT results may still be an improvement over molecular mechanics optimizations, in which essential chemistry is often absent. Thus, we have included the 6-31G/6-31G\*\*<sup>65,66</sup> pairing as a demonstration of the dual-basis method’s ability to capture the polarized double- $\zeta$  basis set regime.

### 3. Results

**3.1. Accuracy.** The DB-SCF gradient for restricted and unrestricted calculations has been implemented in a development version of Q-Chem 3.0.<sup>67</sup> Geometries for 136 open- and closed-shell molecules (167 symmetry-unique bonds),<sup>68</sup> for which experimental equilibrium bond lengths are known, have been computed at several basis set combinations, and results are presented in Tables 1–3. (Only set-wide statistics are reported. The full set of results is available in the Supporting Information.) In all cases, SCF calculations were converged to a maximum DIIS error of  $10^{-8}$  a.u., and integral thresholding was set to  $10^{-12}$  a.u. The convergence criteria for z-vector construction was  $10^{-6}$  a.u. The Q-Chem default geometry optimization tolerances were used:  $3 \times 10^{-4}$  a.u. for maximum gradient component and either  $10^{-6}$  a.u. maximum energy change or  $12 \times 10^{-4}$  maximum displacement between optimization cycles. The following discussion will focus mainly upon the DB-DFT results, for which we have used the common B3LYP<sup>32,33</sup> hybrid functional; DB-HF results will be mentioned when distinct. The SG-1 grid<sup>69</sup> has been used for DFT quadrature integrations.

In the first two columns of these tables, single-basis errors are compared, to demonstrate basis set effects on molecular geometries. Not surprisingly, the effect of polarization functions

**TABLE 2: Errors in Dual-Basis HF Geometries, Relative to Large (Target) Basis Set Geometries in Å<sup>a</sup>**

basis	single basis		dual basis		
	MAD	max	MAD	max	# above 0.01 Å
6-31G/6-31G** <sup>b</sup>	0.0422	0.249	0.0022	0.049	3
6-31G*/6-31++G**	0.0035	0.057	0.0008	0.011	1
6-311G*/6-311++G(3df,3pd)	0.0067	0.042	0.0008	0.007	0
dual[-f]/cc-pVTZ	0.0133 <sup>c</sup>	0.053 <sup>c</sup>	0.0002	0.006	0
dual[-f,-inner d]/cc-pVTZ			0.0009	0.008	0
dual[-f,-2d]/cc-pVTZ			0.0018	0.016	3

<sup>a</sup> MAD = mean absolute deviation; max = maximum absolute deviation. <sup>b</sup> The 6-31G results exclude the ClO molecule, which has a HF bond length of 6.059 Å (1.570 experimental). <sup>c</sup> cc-pVDZ was used as the small basis for comparison in these values.

**TABLE 3: Errors in Dual-Basis B3LYP Geometries, in Å, Relative to 167 Experimental Bond Lengths<sup>a</sup>**

basis	MAD	max
6-31G	0.0516	0.234
6-31G**	0.0146	0.139
6-31G/6-31G**	0.0098	0.075
cc-pVDZ	0.0260	0.261
cc-pVTZ	0.0100	0.072
dual[-f,-inner d]/cc-pVTZ	0.0100	0.077
6-311G*	0.0135	0.115
6-311++G(3df,3pd)	0.0081	0.078
6-311G*/6-311++G(3df,3pd)	0.0083	0.078

<sup>a</sup> MAD = Mean absolute deviation; max = maximum absolute deviation.

(6-31G\*\*) beyond a minimal basis (6-31G) is significant, roughly 0.04 Å. The cc-pVDZ → cc-pVTZ transition produces an average absolute change of 0.019 Å. Even triple- $\zeta$ -plus-polarization geometries are not converged with respect to basis set, as 6-311G\* is still 0.008 Å from the 6-311++G(3df,3pd) results. To put these numbers in context, the average deviation from experiment for these three target basis sets is 0.015 (6-31G\*\*), 0.010 (cc-pVTZ), and 0.008 Å (6-311++G(3df,3pd)). In other words, basis set effects are usually larger than the inherent error of the target basis, with respect to experimental values (again reiterating the fact that B3LYP was parametrized at the complete basis limit).

Errors in dual-basis calculations, with respect to the target basis set, are significantly smaller. For example, the 6-31G/6-31G\*\* pairing reduces the basis set error from 0.039 to only 0.007 Å (and 0.042 to 0.002 Å for HF). Although a reproduction of target basis results would be ideal, the DB-DFT results are still an 82% improvement over small basis calculations for this pairing, and HF improvements are even better. For reference, the MADs relative to experiment are 0.052 Å for 6-31G, 0.015 Å for 6-31G\*\*, and 0.010 Å for 6-31G/6-31G\*\*.

Other basis set pairings show considerable promise, as well. The 6-311G\*/6-311++G(3df,3pd) pairing provides a means of capturing very large basis set effects with only 0.0004 Å average deviation from large basis set geometries. This error is below a common standard 0.001 Å for “chemical accuracy” in calculated geometries and is sufficiently below the target basis error (vs experiment) to conclude that B3LYP/6-311++G(3df,3pd) optimizations may be replaced by their dual-basis counterparts.

The same result is seen for the cc-pVTZ truncation. Although B3LYP/cc-pVTZ geometries are, on average, 0.010 Å from experimental geometries, dual[-f,-inner d]/cc-pVTZ geometries are 0.0005 Å from their large-basis counterparts and subsequently within 0.010 Å of experiment. Thus, we again conclude that dual-basis geometries may replace target basis geometries for cc-pVTZ.

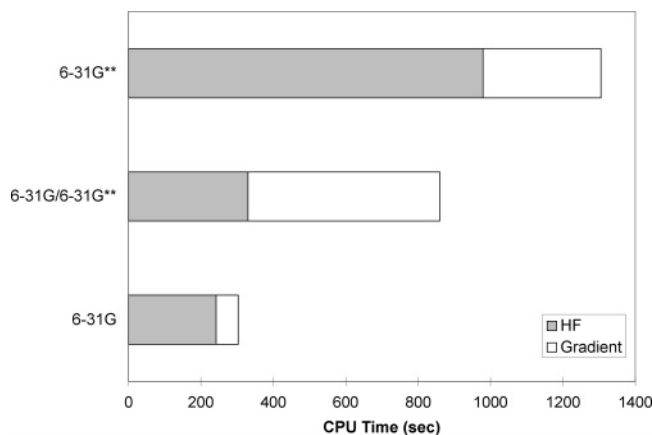
At this point, we recommend the above three pairings for geometry optimizations. Other, more aggressive pairings were

tested, as well, with essentially one conclusion: polarization functions are necessary in the small basis set for quantitative reproduction of target basis results. The results for the 6-31G/6-31G\*\* pairing demonstrate this trend, as errors relative to the target basis are larger than errors for the triple- $\zeta$  pairings. This pairing is retained in the context of errors relative to experiment, however. For the triple- $\zeta$  basis sets, elimination of both sets of *d* functions from cc-pVTZ resulted in average errors of 0.008 Å; this error is still small relative to the error with experimental values (0.019 Å) but does not sufficiently reproduce the target basis geometries. (Interestingly, alternative elimination of the outer *d* function nearly tripled the error, relative to elimination of the inner *d* function.) Similar results hold for the use of 6-311G as a subset of the large Pople-style basis set.

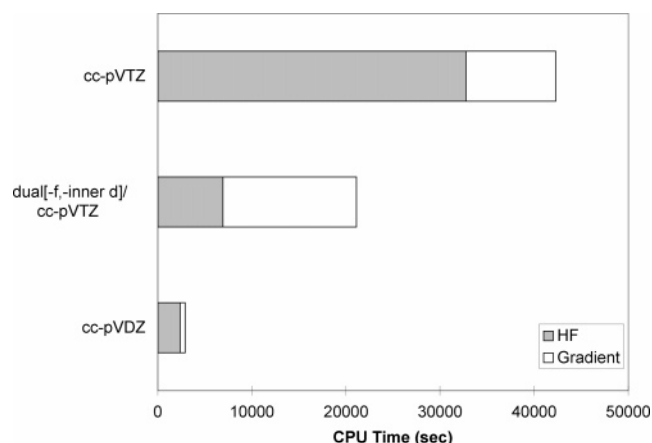
Finally, geometry optimizations in a given basis set are often followed by single-point energy calculations in a larger basis. This practice hinges on the previously mentioned fact that molecular geometries are often less basis set dependent than energies. The dual-basis version of this method was tested on the same set of molecules, as well. For dual-basis 6-311G\*/6-311++G(3df,3pd) energies on 6-31G/6-31G\*\* geometries, absolute energy errors are 0.24 kcal/mol, relative to 6-311++G(3df,3pd) energies on 6-31G\*\* geometries. Additionally, the same comparison was made for dual[-g,-2f]/cc-pVQZ energies on dual[-f,-inner d]/cc-pVTZ geometries. Average absolute energy errors are only 0.026 kcal/mol. Errors in relative energies (conformational energies, reaction energies, etc.) would presumably be even lower. Thus, across both energies and gradients, the dual-basis SCF method provides consistently accurate results. An even more aggressive truncation for B3LYP/cc-pVQZ energies may be possible, as well, such as retaining only the central *d* function. The presented truncation was the subset previously used for DB-MP2 energies.<sup>53</sup>

**3.2. Timings.** To demonstrate the savings possible for a DB-SCF gradient calculation, nuclear force calculations on alanine tetrapeptides, C<sub>12</sub>N<sub>4</sub>O<sub>4</sub>H<sub>22</sub>,<sup>70,71</sup> were computed on a 2 GHz Apple XServe with sufficient memory and a 7200 rpm hard drive. Timings, including energy and gradient breakdowns, are presented in Figures 1–3. The alanine tetrapeptides have roughly the same number of heavy and hydrogen atoms and, thus, represent a reasonably fair comparison, as our truncations for hydrogen are typically more drastic than for heavy atoms. Fullerene-like systems will exhibit less dramatic savings, while saturated hydrocarbons or water clusters, for example, will significantly improve. For reference, the target-to-subset ratio for the three pairings on these systems is 1.83 (6-31G\*\*), 1.98 (cc-pVTZ), and 2.33 (6-311++G(3df,3pd)). The same convergence and threshold settings were used as in the previous section. Also note that incremental Fock builds<sup>72–75</sup> were used in these calculations in order to present DB-HF timings on top of the most efficient available pre-existing code.

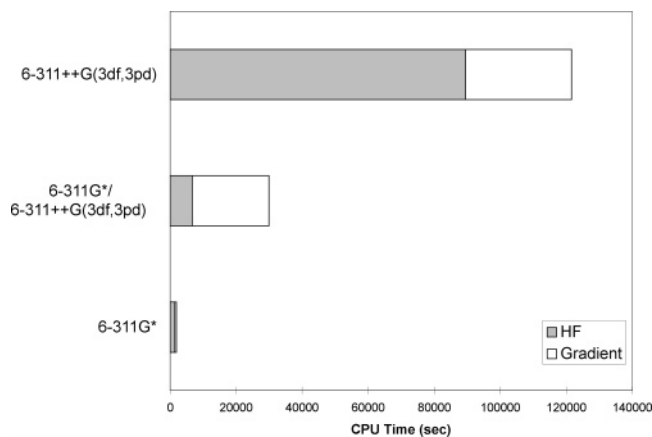
As expected, savings are substantial for the energy portion of a dual-basis force calculation. The 6-31G/6-31G\*\* and



**Figure 1.** Nuclear force timings on a linear alanine tetrapeptide for the 6-31G/6-31G\*\* basis set pairing.



**Figure 2.** Nuclear force timings on a linear alanine tetrapeptide for the dual[-f,-inner d]/cc-pVTZ basis set pairing.



**Figure 3.** Nuclear force timings on a linear alanine tetrapeptide for the 6-311G\*/6-311++G(3df,3pd) basis set pairing.

dual[-f,-inner d]/cc-pVTZ gradients are actually slower than in the target basis, whereas 6-311G\*/6-311++G(3df,3pd) shows noticeable savings in the gradient. Since the gradient is not the majority cost of a standard force calculation, however, the total job times are still reduced for all three pairings.

The small Pople-style pairing essentially represents the worst-case scenario. The DB-HF gradient is 1.6 times longer than the gradient for 6-31G\*\* alone. However, savings in the underlying HF calculation are 66%, resulting in a savings of 34% for the total job. The triple- $\zeta$  pairings demonstrate more promising timings. The dual[-f,-inner d]/cc-pVTZ pairing produces a gradient that is 1.5 times longer than a cc-pVTZ gradient, but

the 85% savings in the HF calculation produce a total job savings of 50%. The 6-311G\*/6-311++G(3df,3pd) pairing demonstrates a 27% speedup in the gradient and a total job savings of 76%. It should be emphasized that an entire DB-HF force calculation can be obtained three times faster than the SCF calculation alone in the target basis for the latter pairing.

#### 4. Conclusions

Analytic gradients for a promising perturbative approach to SCF theory have been derived and implemented. DB-SCF gradients offer savings over standard SCF gradients at many stages of the theory—most notably in  $\Gamma/I^2$ —but the need to solve the CP-SCF equations translates to savings in the gradient alone for large basis set truncations only. A nuclear gradient, however, necessarily requires an underlying SCF calculation, in which significant savings have already been demonstrated. Thus, total job times demonstrate savings of 34–76%. As a rule of thumb, truncations in which the target basis is double the size of the subset produce gradients at identical cost of the target basis and roughly 70% savings in total nuclear force calculations.

Three basis set pairings have been presented. The 6-31G/6-31G\*\* pairing serves as only an approximate reproduction of 6-31G\*\* geometries, with errors of 0.007 Å, although these errors tend to produce geometries (statistically) closer to experimental values. Truncations of triple- $\zeta$  basis sets demonstrate improved performance, in terms of both cost and accuracy, once again placing dual-basis methods most well-suited to the large basis set regime. The larger target basis sets allow for the retention of polarization functions in the smaller basis, a necessary requirement for near-exact reproduction of target basis properties.

Thus, DB-SCF gradients serve as an economical means to obtaining accurate nuclear forces for geometry optimizations and AIMD simulations. For the large basis set regime in particular, in which highly accurate results are obtained and many standard SCF techniques are not completely applicable (linear scaling methods, etc.), DB-SCF gradients provide a viable alternative. In the large-molecule regime, however, these acceleration techniques (as well as RI/DF methods) may still prove worthwhile when coupled with dual-basis methods and may serve as future research topics. Finally, the fact that the CP-SCF equations may be solved in the small basis holds significant promise for related research avenues. The DB/RI-MP2 analytic gradient will be the subject of the forthcoming paired paper, and similar applications to CIS or TD-DFT may prove worthwhile. The DB-SCF Hessian—in which the full set of  $3N$  iterative response equations must be solved—holds particular promise for future work.

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**Supporting Information Available:** A complete list of tabulated geometries, their statistical comparison to experimental geometries, and SAD files for the Dunning subset are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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