1P108   Linear-scaling formation of the Kohn-Sham Hamiltonian: application to the calculation of molecular properties in large molecules

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Recently, we have developed a new code for the linear-scaling formation of the Kohn-Sham Hamiltonian and electronic Hessian for use in generalized-gradient approximation (GGA) density-functional theory (DFT) calculations of molecular properties [1,2].   Our work is implemented in the program system DALTON.   Presently, we present an extension of our code to the inclusion of Hartree-Fock "exact exchange" to enable hybrid-DFT calculations to also be performed.

For the Coulomb contribution, we introduced a new generalization of the fast multipole method (FMM) [3], originally devised for point-charge systems, which allows $O(n)$ calculations over continuous Gaussian distributions.   Our scheme affords a simpler implementation than the original continuous fast multipole method (CFMM) of White $et\ al.$ [4] which was designed for the same purpose.   Our approach differs from their work by introducing a partitioning of the Coulomb energy into "classical" and "nonclassical" terms which may be explicitly evaluated, individually, by linear-scaling multipole techniques and a modified two-electron integral code, respectively.   In this manner, a single FMM-like pass is required for the evaluation of the classical Coulomb energy in which continuous, possibly overlapping, Gaussian distributions are treated like point-charges; this is followed by a nonclassical correction phase in which the overlap effects are computed explicitly and added to the classical contribution.   We name our algorithm the branch-free multipole method (BFMM) since it can be regarded as a generalization of the original FMM that does not require the additional book-keeping structures ("branches") introduced in the CFMM algorithm.

For the exact exchange contribution, our approach follows the pioneering work of Schwegler and Challacombe [5] in which the linear-scaling regime may be achieved by exploiting the sparsity of the density matrix.   For electrically insulating materials, for example, Kohn has shown [6] that the density matrix elements fall off exponentially in the following manner

$$\rho(\mathbf{r}_1, \mathbf{r}_2) \sim e^{-\kappa |\mathbf{r}_1 - \mathbf{r}_2|}$$

as $|\mathbf{r}_1\text{-}\mathbf{r}_2| \rightarrow \infty$, where κ is a constant characteristic of the system (related to the band-gap).   By pre-ordering integral estimates and employing efficient testing, the ONX algorithm of Schwegler $et\ al.$ [7] may achieve effective linear-scaling, but for small-gap systems with long-range (real-space) exchange contributions the algorithm reverts to the quadratic-scaling regime.   Our algorithm also relies on the fundamental sparsity of the density matrix, but our implementation differs from their work, and also the successful $O(n)$ LinK scheme of Ochsenfeld $et\ al.$ [8], in the following manner.

In the present work, we again exploit the partitioning of the two-electron integrals into "classical" and "nonclassical" parts.   In this way, the computational work with super-linear scaling is conceptually isolated in the classical phase: for both Coulomb and exchange, the nonclassical phase is automatically linearly scaling.   Specifically, given that all integrals over Gaussian basis functions may be expressed as linear combinations of Boys functions, $F_n(x)$, of orders $n \geq 0$, we introduce the following decomposition

$$F_n(x) = \int_0^1 \exp(-xt^2)t^{2n}dt = F_n^{\mathrm{cls}}(x) + F_n^{\mathrm{non}}(x)$$

where the classical contribution may be defined by

$$F_n^{\mathrm{cls}}(x) = \int_0^\infty \exp(-xt^2)t^{2n}dt = \frac{(2n-1)!!}{2^{n+1}}\sqrt{\frac{\pi}{x^{2n+1}}} > 0$$

and the nonclassical correction term by

$$F_n^{\text{non}}(x) = -\int_1^\infty \exp(-xt^2)t^{2n}dt = -\frac{1}{2}E_{1/2-n}(x) < 0$$

where $E_n(x)$ is the exponential integral function

$$E_n(x) = \int_1^\infty \exp(-xt)t^{-n}dt = x^{-1}\exp(-x)\left[1 + O(x^{-1})\right]$$

The argument x is given by

$$\frac{pq}{p+q}R_{PQ}^2$$

where p and q are the exponents of the Gaussian distributions, and R_{PQ} the separation between their centres. Clearly, the negative nonclassical contribution, which decays exponentially in R_{PQ}, will rapidly enter the linear-scaling regime as R_{PQ} becomes large on the molecular scale. In contrast, the classical contribution is non-local, but may be treated completely using multipole acceleration techniques.

This approach is conceptually attractive and, in addition, removes all need for the elaborate consideration of "penetration acceptability criteria" over which many authors have devoted considerable thought (e.g. ref.[9]). In principle, *all* charge interactions may be treated by multipole expansion in our scheme, with the corrections due to $E_n(x)$ applied afterwards. Moreover, the decay of $E_n(x)$ is seen to be *independent* of n – that is, the screening of the nonclassical integrals can be implemented in a rigorous and simple manner that is *independent of the angular momentum* of the basis functions. (This should be contrasted with tests based on Gaussian overlap, ubiquitous in the literature, where often a simple "s-s" overlap test is used in an *ad hoc* manner for all higher angular momentum functions also).

In the case of the Coulomb energy, the non-local term is efficiently treated using the FMM as described above. This cannot be applied to the exchange problem, but the use of efficient multipole expansion techniques is still employed. We note that Schwegler and Challacombe [9] have previously presented an implementation of their ONX algorithm combined with multipole expansions for the long-range integrals. However, we emphasize that they do not exploit the explicit partitioning of the classical and nonclassical terms that we favour and only contract integrals of "well-separated" Gaussians (with a negligible nonclassical component, according to some "acceptability criteria") using multipole techniques. By removing the need for these complex acceptability criteria, we argue that our approach is simpler than the traditional schemes.

These techniques have also been implemented for the construction of the electronic Hessian for the calculation of molecular properties using linear response theory. As a result, the traditional bottlenecks for the treatment of second-order static and dynamic properties in large molecular systems have been removed. We demonstrate the capabilities of our code with some timing benchmarks, as well as applications to the calculation of electric and magnetic properties, using both GGA and hybrid DFT functionals.

References

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