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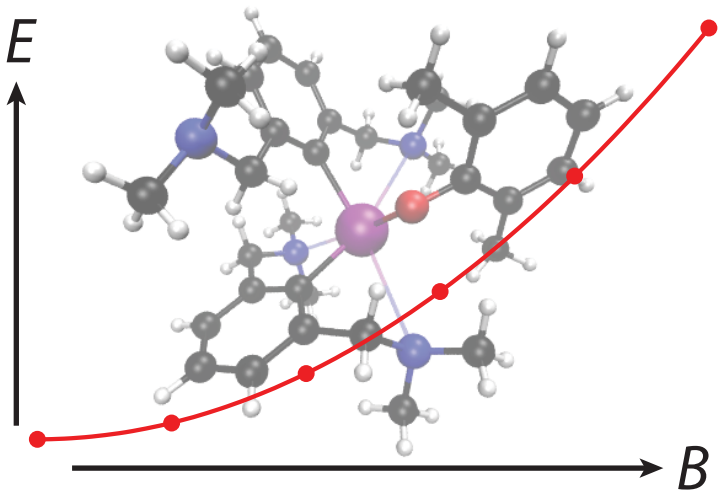
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Dirac-Hartree-Fock (GIAO)



Four-component Dirac–Hartree–Fock method with gauge-including atomic orbitals.

Fully relativistic self-consistent field under a magnetic field[†]

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Received Xth XXXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXXXX 200X

DOI: 10.1039/b000000x

We present a gauge-invariant implementation of the four-component Dirac–Hartree–Fock method for simulating the electronic structure of heavy element complexes in magnetic fields. The additional cost associated with the magnetic field is shown to be only 10–13% of that at zero field. The Dirac–Hartree–Fock wave function is constructed from gauge-including atomic orbitals. The so-called restricted magnetic balance is used to generate 2-spinor basis functions for the small component. The molecular integrals for the Coulomb and Gaunt interactions are computed using density fitting. Our efficient, parallel implementation allows for simulating the electronic structure of molecules containing more than 100 atoms with a few heavy elements under magnetic fields.

Properties of molecules under an external magnetic field have been extensively studied in recent experiments. For instance, external magnetic fields can suppress quantum tunneling between different m_s states in the ground spin manifold of field-induced single-molecule magnets, resulting in slow magnetic relaxation.¹ When simulating the electronic structure of molecules under magnetic fields, however, conventional finite basis expansions are plagued by non-physical dependence on the choice of gauge origin.² This problem can be solved by introducing the gauge-including atomic orbitals (GIAOs), also called London orbitals.^{3–6} A GIAO is a standard atom-centered Gaussian basis function ϕ_r^g multiplied by a plane wave,

$$\phi_r(\mathbf{r}; \mathbf{A}, \mathcal{B}) = \phi_r^g(\mathbf{r}; \mathbf{A}) \exp(-i\mathcal{A}(\mathbf{A}) \cdot \mathbf{r}), \quad (1)$$

where $\mathcal{A}(\mathbf{A})$ is the vector potential at the center of the function \mathbf{A} . In the Coulomb gauge, the vector potential of a uniform magnetic field \mathcal{B} is given by

$$\mathcal{A}(\mathbf{r}) = \frac{1}{2} \mathcal{B} \times (\mathbf{r} - \mathbf{r}_G), \quad (2)$$

[†] Electronic Supplementary Information (ESI) available: Algorithms for integral evaluation, isotropic and anisotropic magnetizabilities, wall-clock times for Dirac–Hartree–Fock calculations with the Gaunt interaction, converged energies, and coordinates used for timing analysis. See DOI: 10.1039/b000000x/

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where \mathbf{r}_G is the gauge origin.

Gauge-invariant methods based on GIAOs have been developed for magnetic properties such as NMR shielding tensors,^{2,6–13} magnetizabilities,^{14–16} hypermagnetizabilities,¹⁷ rotational g -tensors,^{16,18} and induced ring currents.^{19,20} Most previous studies have been based on linear response approaches,²¹ which determine the properties as the derivatives of energy with respect to field strength at zero field. An exception is the work of Tellgren and co-workers,^{17,22–24} which demonstrated the non-linear response of closed-shell paramagnets to intense magnetic fields.

In this work, we present a non-perturbative, gauge-invariant implementation of the four-component Dirac–Hartree–Fock method for molecules in magnetic fields using the Dirac–Coulomb–Gaunt Hamiltonian,

$$\hat{H} = \sum_i \left[c^2(\beta - I_4) + c(\alpha \cdot \hat{\pi}_i) - \sum_A^{\text{atoms}} \frac{Z_A}{r_{iA}} \text{erf}(\sqrt{\zeta_A} r_{iA}) \right] + \sum_{i < j} \left[\frac{1}{r_{ij}} - \frac{\alpha_i \cdot \alpha_j}{r_{ij}} \right], \quad (3)$$

where c is the speed of light, α and β are the 4×4 Dirac matrices, and I_4 is the identity matrix. Using SI-based atomic units, the momentum operator $\hat{\pi}_i$ is given by

$$\hat{\pi}_i = -i\nabla_i + \mathcal{A}(\mathbf{r}_i). \quad (4)$$

The nuclear attraction operator in Eq. (3) corresponds to a Gaussian model for the nuclear charge Z_A with exponent ζ_A .

We use 2-spinor basis functions throughout this work. The small-component basis functions Φ_r^{S+} and Φ_r^{S-} are generated by applying restricted magnetic balance^{25,26} (RMB) to the large-component spinors:

$$\Phi_r^{S\pm} = \frac{1}{2c} \alpha \cdot \hat{\pi} \Phi_r^{L\pm}, \quad (5)$$

where the large-component basis functions Φ_r^{L+} and Φ_r^{L-} are scalar GIAOs [*i.e.*, $(\phi_r, 0, 0, 0)^T$ and $(0, \phi_r, 0, 0)^T$]. An RMB basis set not only prevents variational collapse but also ensures that the Pauli equation is obtained at the non-relativistic limit.^{26,27} With this basis, the Fock matrix is constructed using the algorithm described in Ref.²⁸, which is applicable to open-

Table 1 Errors due to density fitting in Dirac–Hartree–Fock calculations with a magnetic field (in mE_h). Reference energies were computed with a large even-tempered fitting basis set and listed in E_h .

Hamiltonian	B/T		TZ-JKFIT	QZ-JKFIT	5Z-JKFIT	TZ-JKFIT+1	QZ-JKFIT+1	5Z-JKFIT+1	Even-temp
Br ₂ / cc-pVDZ									
Coulomb	0		0.077	0.049	0.033	0.031	0.029	0.024	−5205.836949
Coulomb	1×10^4	⊥	0.079	0.049	0.034	0.031	0.029	0.024	−5205.826608
Coulomb	1×10^4	∥	0.077	0.049	0.033	0.031	0.029	0.024	−5205.824547
Coulomb–Gaunt	0		−27.341	−27.396	−27.358	0.019	0.017	0.013	−5203.165566
Coulomb–Gaunt	1×10^4	⊥	−27.339	−27.396	−27.358	0.019	0.017	0.013	−5203.155213
Coulomb–Gaunt	1×10^4	∥	−27.341	−27.396	−27.358	0.019	0.017	0.013	−5203.153153
Se ₂ / cc-pVDZ									
Coulomb	1×10^4	∥	0.117	0.079	0.050	0.051	0.047	0.041	−4853.712062
Coulomb–Gaunt	1×10^4	∥	−24.455	−24.500	−24.486	0.035	0.030	0.024	−4851.288051

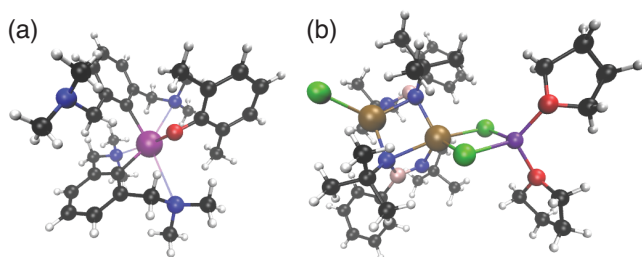


Fig. 1 Molecules used for the timing benchmarks in this work: (a) $C_{32}H_{47}BiN_4O$ and (b) $C_{36}H_{62}B_2Cl_3In_2LiN_4O_2$.

and closed-shell molecules. Molecular integrals over GIAOs are evaluated using algorithms analogous to those developed for Gaussian orbitals.²⁹ Rys quadrature is used with complex parameters for the electron repulsion and nuclear attraction integrals, in which quadrature roots and weights are tabulated in a two-dimensional table at compile time and interpolated at runtime. The working equations for these integrals as well as a discussion of numerical stability are provided in the ESI.

Our algorithm uses density fitting, which approximates a 4-index integral as a linear combination of products of 2- and 3-index integrals by expanding an orbital pair in real auxiliary functions χ_γ as

$$\phi_r^*(\mathbf{r})\phi_i(\mathbf{r}) \approx \sum_{\gamma} C_{\gamma}^{ri} \chi_{\gamma}(\mathbf{r}). \quad (6)$$

Here ϕ_i and ϕ_r are occupied and general GIAOs. The expansion coefficients C_{γ}^{ri} are optimized by minimizing the fitting errors in the Coulomb metric.³⁰ Though an expansion with auxiliary GIAOs is also valid, we use real auxiliary functions for efficiency. The same approach has been used for computing NMR chemical shifts.^{10,12,13}

Fitting errors in the energy are presented for Br₂ (singlet) and Se₂ (triplet) in Table 1. The bond lengths were set to

2.3218 Å and 2.1660 Å, respectively. The cc-pVDZ basis set was used.³¹ Reference energies were computed using a large even-tempered fitting basis ($21s21p21d21f21g21h21i$) as described in Ref.²⁸. The nuclear charge distributions tabulated by Visscher and Dyall were used.³² We used the standard JKFIT auxiliary basis sets³³ and the customized “JKFIT+1” basis sets that contain tighter functions in the p , d , and f shells.²⁸ The increased errors with the Gaunt interaction using the standard fitting basis sets are due to the fitting of products of large- and small-component orbitals, which require tight higher-angular momentum fitting functions.²⁸ The errors were almost identical to those at zero field, allowing for accurate computation of magnetic properties using numerical differentiation with respect to field strength.

The wall-clock times for Hartree–Fock calculations with the non-relativistic and Dirac–Coulomb Hamiltonians on the molecules depicted in Fig. 1 are presented in Fig. 2. Those for calculations with the Gaunt interaction are reported in the ESI. The two molecules in Fig. 1 have been investigated in separation³⁴ and boraamidate coordination chemistry.³⁵ The def2-SVP basis set³⁶ was used except for Bi and In, for which we used Dyall’s uncontracted double- ζ basis set.^{37,38} The numbers of basis functions were 963 and 1231 for molecules (a) and (b), respectively. For the fitting basis set, we combined the def2-TZVPP-JKFIT basis set³⁹ for light atoms with Dyall’s uncontracted double- ζ basis set extended by applying the d and f exponents to higher angular shells up to i for In and Bi, respectively. Tests were run using the experimental geometries,^{34,35} which can be found in the ESI. The timings were measured on a cluster of Xeon E5-2650 2.00GHz (1024 CPU cores) with InfiniBand QDR. Integral evaluation over GIAOs is more costly than over real Gaussian functions due to the need for two-dimensional interpolation in the computation of electron repulsion integrals. Another dominant step is inversion of fitting metric, which is unaffected by the introduction of magnetic field. In all cases, integral evaluation for

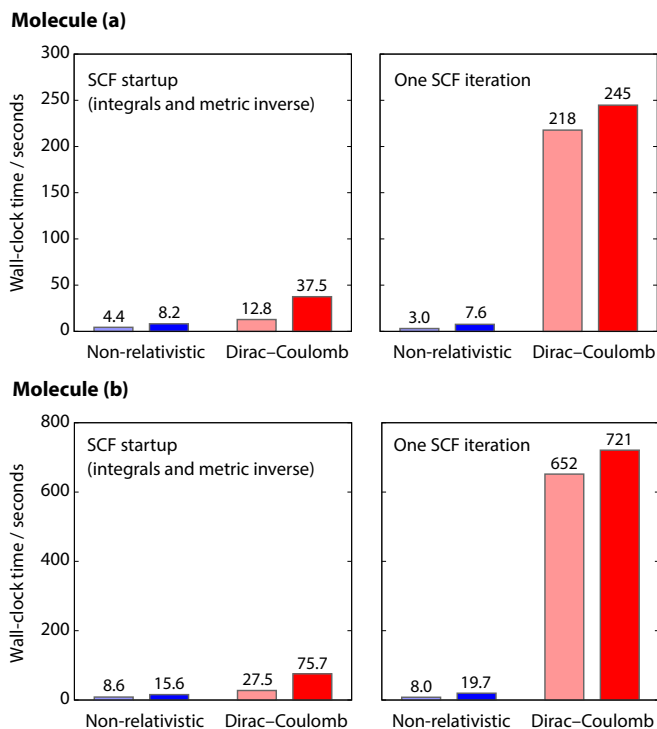


Fig. 2 Wall-clock times for the Hartree-Fock method with the nonrelativistic and Dirac-Coulomb Hamiltonians without (light colors) and with (dark colors) a magnetic field. These benchmarks used a double- ζ basis set and were run using 1024 CPU cores.

Dirac-Hartree-Fock required less than 20% of the time for a single self-consistent iteration. Each iteration with GIAOs took only 10–13% longer than that at zero field. The small difference originates from the transformation of the complex 3-index GIAO integrals to half-transformed molecular integrals. The computational costs for the other steps are identical with and without a magnetic field, since both deal with complex tensors of the same size. This is in contrast to the non-relativistic counterpart, where the use of GIAOs more than doubles the computational cost. Figure 3 illustrates a smooth, quadratic energy curve of $C_{32}H_{47}BiN_4O$ [molecule (a)] around zero field as a function of field strength. Results are shown with the def2-SVP basis set for light atoms and Dyal's uncontracted double- ζ basis set for Bi. As a comparison, we have also shown those with Dyal's contracted double- ζ basis set (spin-free, valence flexibility) for Bi. Note that relativistic calculations with the contracted basis set indicated an artificial paramagnetic response, reiterating the need for a flexible basis set.

We also calculated isotropic magnetizabilities of NF_3 , AsF_3 , and BiF_3 using a 7-point finite-difference formula (Fig. 4). The results were compared to those reported by Iliáš *et al.*,¹⁵ in which the linear response approach was em-

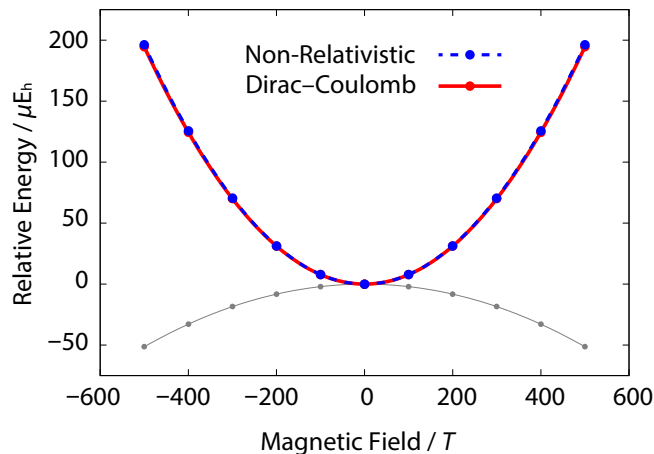


Fig. 3 Hartree-Fock energies of $C_{32}H_{47}BiN_4O$ as a function of magnetic field strength with quadratic curve fits. The relativistic energies with Dyal's contracted double- ζ basis set are shown in gray. Non-relativistic energies are indistinguishable with and without basis-set contraction.

ployed with the so-called simple magnetic balance (sMB).⁴⁰ Dunning's correlation-consistent basis sets were used for F, N, and As,³¹ and Dyal's double- ζ basis set for Bi.^{37,38} All basis sets were used in their uncontracted forms with a large fitting basis (i.e., the fitting errors are negligible; see the ESI for details). The molecular geometries can be found in Ref.¹⁵. The basis-set convergence of magnetizabilities is almost parallel to that obtained by non-relativistic Hartree-Fock, attesting to the effectiveness of RMB. The contributions from the Gaunt interaction were marginal in these examples.

In conclusion, we have presented an efficient and gauge-invariant implementation of the Dirac-Hartree-Fock method with RMB that is applicable to large molecules under magnetic fields. The program is available in the open-source BAGEL package.⁴¹ We have shown that the additional computational costs associated with the magnetic field are marginal, making the method applicable to molecules of more than 100 atoms and several heavy elements. The errors due to density fitting are almost constant with and without the magnetic field, allowing us to accurately compute magnetic properties using finite-difference formulas. This work is a step toward realizing the multi-configurational treatment of magnetic molecules containing heavy elements interacting with magnetic fields.

Acknowledgements

The authors thank an anonymous referee for valuable comments. This work has been supported by the National Science Foundation CAREER Award (CHE-1351598).

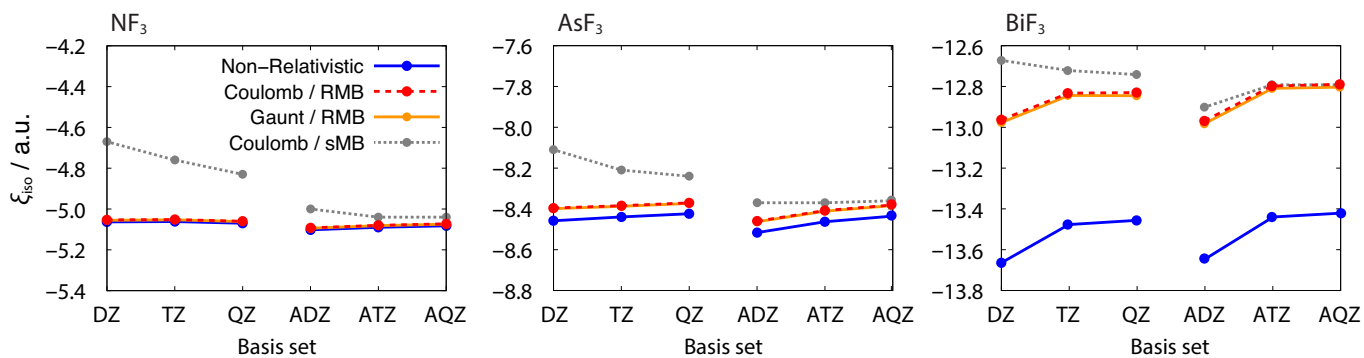


Fig. 4 Convergence of isotropic magnetizabilities (ξ_{iso}) for NF_3 , AsF_3 , and BiF_3 with respect to basis set size. The results with SMB were taken from Ref. ¹⁵.

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