Scalar-relativistic linear combinations of Gaussian-type-orbitals technique for crystalline solids

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The first nonperturbative implementation of scalar relativity in an all-electron linear combinations of Gaussian-type-orbitals methodology for crystalline solids is reported. Test calculations on fcc gold yield bulk and one-electron properties that are indistinguishable from results obtained with other all-electron, scalar-relativistic density-functional techniques. This development paves the way for joint cluster and crystalline calculations on heavy-atom systems using a single all-electron, full-potential technique. [S0163-1829(98)04212-X]

The linear combinations of Gaussian-type-orbitals–fitting function (LCGTO-FF) technique is routinely used to perform all-electron, full-potential, density-functional theory (DFT) electronic-structure calculations on a wide range of systems, including isolated clusters of atoms,[1] one-dimensional (1D) periodic polymer chains,[2] 2D periodic films,[3] and crystalline solids.[4] This ability to treat periodically extended (crystalline) and localized (molecular) systems on an equal footing is one of the primary advantages of the LCGTO-FF method over other existing DFT electronic-structure techniques. To this extent, the LCGTO-FF method may be viewed as a ''universal'' methodology that bridges the often wide gap between solid-state physics and quantum chemistry. There is a growing need for such a methodology, since many of the systems that are of the greatest current technological interest do not lie entirely within the scope of either discipline and may be best investigated with an algorithmically consistent combination of local and extended calculations; e.g., nanostructures on a surface, heterogeneous catalysts, etc.

The value of the LCGTO-FF technique as a ''universal'' DFT electronic-structure methodology has been somewhat abridged thus far by the absence of any stable technique for incorporating relativistic effects during calculations on systems that include heavy atoms.[5] This shortcoming, which afflicts nearly all of the fixed-basis-set methods commonly used in quantum chemistry, has long provided one of the great challenges facing computational chemists (and those solid-state physicists who employ similar techniques). Although numerous strategies have been suggested over the years for incorporating relativistic effects into all-electron fixed-basis-set calculations,[5] most practical calculations to date have been forced to rely on either perturbation theory or some form of relativistic pseudopotential.

A major breakthrough on this venerable problem occurred recently when Häberlen and Rösch[6] (HR) demonstrated the feasibility of carrying out scalar-relativistic LCGTO-FF calculations on heavy-atom clusters using an ''incomplete'' Douglas-Kroll-Hess[7–9] transformation; hereafter, the HR approximation. Since that time, the scalar-relativistic LCGTO-FF cluster technique has been applied to a number of systems containing heavy atoms with apparent success.[10] Verification of the validity of those results has been hindered, however, by the absence of previous all-electron, full-potential, scalar relativistic DFT calculations with which to

compare. For this reason, it is not entirely clear at this time that the version of scalar relativity being used in the cluster calculations is directly comparable with the Koelling-Harmon[11] implementation of scalar relativity that is used in most solid-state DFT codes.

In the present work, the HR approximation has been used to implement scalar-relativity in an existing computer program (GTOFF) (Ref. 4) designed to perform LCGTO-FF calculations on crystalline solids and thin films. GTOFF has then been used to perform the first all-electron, scalar-relativistic LCGTO calculation on a crystalline solid; gold (Au; $Z=79$). Since Au has been studied previously with other scalar-relativistic DFT electronic-structure techniques,[12–15] the present results provide the first direct comparison between the HR and Koelling-Harmon formulations of scalar-relativity, to our knowledge. This work thus represents an essential step in the development of an all-electron, full-potential electronic structure technique capable of treating heavy-atom clusters and crystalline solids on an equal footing.

The development of the scalar-relativistic DFT methodology used by HR (Ref. 6) begins with the four-component Dirac-Kohn-Sham (DKS) equations,[16]

$$h_{\mathrm{DKS}}^{(4)} \psi_i = [(c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta m c^2) + v_{\mathrm{eff}}] \psi_i = \epsilon_i \psi_i, \qquad (1)$$

where

$$v_{\mathrm{eff}} = v_n + v_c + v_{\mathrm{xc}}, \qquad (2)$$

is the effective one-electron potential formed from the nuclear potential v_n, the classical electronic Coulomb potential v_c, and the DFT exchange-correlation (XC) potential v_{xc}. The eigenvalues of the DKS equations are unbounded, above and below, since they include both electron and positron degrees of freedom. Therefore, any attempt to solve the DKS equations variationally will lead to the well-known ''variational collapse'' problem, unless the freedom of the basis set used is carefully restricted.[5] This difficulty can be circumvented by performing some unitary transformation on the DKS equations that approximately decouples the electron and positron degrees of freedom. For example, it is well known that the DKS equations can be decoupled to arbitrary order in $(\mathbf{p}/mc)^2$ via a series of Foldy-Wouthuysen[17] transformations. Unfortunately, the Foldy-Wouthuysen procedure

produces operators that are highly singular at the nucleus, and, hence, not amenable to an all-electron variational solution. Traditional scalar-relativistic solid-state electronic-structure techniques[12–15] avoid these difficulties by first obtaining the core orbitals as numerical solutions to a spherically symmetric, quasiatomic, differential equation and then requiring the valence orbitals to be orthogonal to those core states, effectively restricting their variational freedom near the nucleus. Such a solution is not feasible for a fixed-basis-set methodology (like LCGTO-FF) that treats the core and valence electrons on an equal footing.

An alternative approach, which does not generate singular operators, uses the Douglas-Kroll-Hess transformation[7–9] to decouple the DKS equations to second order in the external-field v_{eff}. This procedure yields the two-component, external-field projector (EFP) equations

$$h^{(2)}_{EFP}\phi_i = \epsilon_i\phi_i, \tag{3}$$

$$h^{(2)}_{EFP} = E_p + A_p[v_{eff} + R_p v_{eff} R_p]A_p - \tfrac{1}{2}(E_p W^2 + W^2 E_p + 2WE_p W),$$

where

$$E_p = c(p^2 + m^2 c^2)^{1/2}. \tag{4}$$

$$A_p = \left[\frac{E_p + mc^2}{2E_p}\right]^{1/2}, \tag{5}$$

$$R_p = K_p \boldsymbol{\sigma}\cdot\mathbf{p}, \tag{6}$$

$$K_p = c/(E_p + mc^2), \tag{7}$$

and W can be expressed in momentum space as

$$W_{p,p'} = A_p(R_p - R_{p'})A_{p'}\left[\frac{v_{eff}(\mathbf{p},\mathbf{p}')}{E_p + E_{p'}}\right], \tag{8}$$

where $v_{eff}(\mathbf{p},\mathbf{p}')$ is the momentum-space representation of v_{eff}. As written, the EFP equations are fully relativistic, in the sense that they include mass-velocity, Darwin, and spin-orbit coupling corrections. Throughout the remainder of this work, it will be assumed that all of the spin-orbit coupling terms in Eq. (3) are neglected to obtain the scalar-relativistic EFP approximation. (A detailed discussion of the separation of the relativistic corrections into scalar-relativistic and spin-orbit coupling terms has been presented elsewhere,[18] and will not be repeated here.)

Analytical evaluation of the GTO matrix elements for the momentum-space operators in Eq. (3) has not proven to be practical thus far. This difficulty can be circumvented by using an approximate momentum-space representation obtained by diagonalizing the nonrelativistic kinetic-energy matrix.[19] First, the matrix elements of $\mathbf{p}\cdot v\mathbf{p}$ and $\mathbf{p}\times v\mathbf{p}$ (which are required even for scalar-relativistic EFP calculations) are evaluated along with the usual nonrelativistic matrix elements. Next, the nonrelativistic kinetic-energy matrix is diagonalized to obtain approximate eigenfunctions of p^2, and all the matrices are transformed to this approximate momentum space. Since the operators E_p, A_p, and K_p are diagonal in momentum space, they can be obtained trivially from the p^2 eigenvalues. These basic components are then

used to build the more complicated matrix elements needed, such as $A_p R_p v R_p A_p$. Finally, all of the matrices are back-transformed to the original GTO representation.

The most serious drawback to the procedure described above is that the transformations for the two-electron integrals are very demanding computationally. HR found that they could achieve a substantial reduction in the resources required for their calculations by using an ''incomplete'' Douglas-Kroll-Hess transformation which only affects the kinetic-energy and nuclear potential terms in the DKS equations. They also dropped all terms in the resulting EFP equation that involved $\mathbf{p}\times v_n\mathbf{p}$. A recent series of test calculations on isolated atoms[18] found that the HR approximation produces one-electron eigenvalues for the chemically active valence states that differ little from those obtained with the complete scalar relativistic Douglas-Kroll-Hess transformation.

The present implementation of HR scalar-relativity in GTOFF was tested by carrying out a series of nonrelativistic and scalar-relativistic calculations on fcc Au. The calculations employed a very rich $20s16p12d8f$ primitive orbital basis set, derived from Gropen's[20] $19s14p10d5f$ atomic basis, which was very loosely contracted into $15s12p9d4f$ scalar-relativistic and nonrelativistic orbital basis sets using coefficients obtained from paramagnetic atom calculations. The electron density was fitted variationally with 18 s-type GTO's, while the XC integral kernels were least squares fitted with 15 s-type GTO's.[21] The local-density approximation (LDA) XC parametrization of Hedin and Lundqvist[22] was employed for all of the calculations. All Brillouin zone (BZ) integrations were carried out on a uniform $8\times8\times8$ mesh with 29 irreducible $\mathbf{k}$ points using a Gaussian broadening of 20 m Ry. Test calculations using a sparser $6\times6\times6$ mesh with 16 irreducible points indicate that the present results are well converged with respect to the BZ mesh density. The self-consistent-field cycle was iterated until the total energy was converged to less than 0.01 m Ry.

Total energies and electronic band structures were calculated scalar relativistically at six lattice constants ranging from 7.4 to 7.9 bohr, and nonrelativistically at six lattice constants ranging from 7.8 to 8.3 bohr. In each case, cohesive energies were obtained by subtracting the total energy of an isolated, spin-polarized atom. The cohesive energies were then fitted with a modified version of the universal equation of state[23] to obtain the zero-pressure lattice constant a_0, bulk modulus B, and pressure derivative of the bulk modulus B' for fcc Au. The standard deviations for the fits were both less than 4 μ Ry, demonstrating the good numerical stability achieved with GTOFF.

The nonrelativistic and scalar-relativistic LCGTO-FF results obtained here are compared in Table I with results from three previous all-electron, full-potential scalar-relativistic calculations using either the full-potential linearized augmented-plane-wave (FLAPW) method[13,15] or the full-potential linearized muffin-tin-orbital (FLMTO) method.[14] Also shown are the experimental values listed in Ref. 13. Comparison of the nonrelativistic and scalar-relativistic LCGTO-FF results reveals the large impact that relativity has on the lattice constant (6%) and bulk modulus (57%) of fcc Au. In comparison, the differences between the various scalar-relativistic results in Table I are quite small. In fact,

TABLE I. The lattice constant (a_0; bohr), bulk modulus (B; GPa), and pressure derivative of the bulk modulus (B') for fcc Au obtained here with nonrelativistic (NR) and scalar-relativistic (SR) LCGTO-FF calculations are compared with previous all-electron, full-potential scalar-relativistic calculations and experimental values quoted by Ref. 13.

	Source	a_0	B	B'
NR LCGTO-FF	Present	8.077	112	5.62
SR LCGTO-FF	Present	7.633	196	5.49
SR FLAPW	Ref. 13	7.66	198	
SR FLMTO	Ref. 14	7.68	193	
SR FLAPW	Ref. 15	7.67	205	
Experiment	Ref. 13	7.67	172	

TABLE II. Band energies for fcc Au from nonrelativistic (NR) and scalar-relativistic (SR) LCGTO-FF calculations ($a = 7.70$ bohr) are compared with results from a scalar-relativistic APW calculation (Ref. 12). All-energies are given in eV relative to the Fermi energy. (E_{sb}, bottom of the s band; E_{db}, bottom of the d band; E_{dt}, top of the d band.)

	E_{sb}	E_{db}	E_{dt}
NR LCGTO-FF	8.35	8.11	3.10
SR LCGTO-FF	10.01	7.44	1.59
SR APW	9.92	7.22	1.33

the $0.4 \rightarrow 0.6\%$ reduction in the LCGTO-FF lattice constant relative to the other calculations may simply be due to the substantially richer orbital basis set employed here. The present scalar-relativistic LCGTO-FF result for a_0 exhibits the expected LDA-induced lattice contraction relative to the experimental value.

An additional nonrelativistic LCGTO-FF calculation was carried out at a lattice constant of 7.7 bohr to allow a direct comparison of the scalar-relativistic and nonrelativistic one-electron eigenvalues near the experimental equilibrium. Three particularly interesting locations in the occupied band structure of Au are the bottom of the s band (E_{sb}; at Γ), the bottom of the d bands (E_{db}; at L or X), and the top of the d bands (E_{dt}; at W); for a more detailed discussion of the band structure of fcc Au, see Ref. 12. In Table II the current nonrelativistic and scalar-relativistic LCGTO-FF results for these three band-energies, relative to the Fermi energy, are compared with results from an earlier scalar-relativistic APW calculation.[12] (Unfortunately, the full-potential calculations did not list any eigenvalues with which to compare.[13-15]) Once again, comparison of the nonrelativistic and scalar-relativistic results reveals large relativistic effects on fcc Au. The most important qualitative change in the band

structure is a more than 2-eV lowering of the s band relative to the bottom of the d bands. In addition, the overall width of the d bands is increased by more than 15% due to a relativistic delocalization of the d states. The small differences between the two sets of scalar-relativistic results in Table II are no greater than would be expected given the differences between the methods used; full-potential LCGTO-FF vs muffin-tin APW.

The results presented in Tables I and II clearly demonstrate that the HR scalar-relativistic LCGTO-FF technique, as implemented in GTOFF, produces results that are nearly indistinguishable from the results obtained with other all-electron, scalar-relativistic DFT electronic-structure techniques.[12-15] The current results therefore provide support for the overall reliability of the heavy-atom cluster calculations that have already been carried out using the HR approximation. In addition, the HR approximation must now be viewed as a viable, and fully independent, alternative to the implementation of scalar relativity[11] used in most other solid-state electronic-structure codes. Based on these results, it should be possible to carry out the first joint solid-state physics and quantum-chemistry calculations on heavy-atom systems (including films and polymers) using a single all-electron, full-potential electronic-structure technique.

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