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LETTER TO THE EDITOR

Correlation functional estimates of the dispersion interaction in semi-ionic compounds

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Abstract. We extend a recent *ab initio* investigation of the structure and energetics of β-$MgCl_2$ to include correlation functional estimates of the dispersion interaction between the anions. We examine the performance of functionals with and without gradient corrections based on parameterizations of the homogeneous electron gas and studies of the helium atom. We find that gradient corrected correlation functionals provide a surprisingly accurate description of the dispersion interaction near equilibrium.

Hartree–Fock (HF) theory has been applied to problems concerning the structural energetics of insulators and semiconductors with great success (Orlando *et al* 1990, Pisani *et al* 1988). The accuracy of such calculations is limited by the choice of basis set in which the wavefunction is expanded, the numerical precision with which the SCF equations are solved and the HF approximation itself. To a large extent the implementation of the HF theory in the CRYSTAL package has overcome the problems associated with the choice of basis set and numerical accuracy (Pisani *et al* 1988, Dovesi *et al* 1988, 1992). One is thus able to address the deficiencies of the HF approximation directly.

In a recent paper we examined in detail the structural energetics of β-$MgCl_2$ at the HF level (Harrison and Saunders 1992); this paper will be referred to as HS1. β-$MgCl_2$ has the trigonal $P\overline{3}m1$ space group; the hexagonal primitive cell is defined by the structural parameters c and a. The fractional coordinate u positions the plane of chlorine ions relative to the magnesium layers. The layered structure is favoured relative to the ionically stabilized rutile structure because of the strong polarization of the anion and the formation of weak covalent bonds (HS1). The stability of the structure with respect to a distortion which separates the Cl–Mg–Cl layers was found to be dependent upon the introduction of an empirical ‘dispersion’ interaction between the anions. Within HF theory the compound is unstable with respect to this distortion. The current work is concerned with the use of the local density approximation to density functional theory (LDA) to estimate the correlation corrections to HF. There have been several attempts to develop a correlation-only functional for this purpose which have lead to excellent results (Orlando *et al* 1990). Such functionals are based upon accurate treatments of the electron gas in various prototypical environments. The simulations of the homogeneous electron gas by Ceperly and Alder

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(1986) have been fitted by Vosko *et al* (1980) and Perdew and Zunger (1981) to produce functionals that we refer to as VWN and PZ respectively. Refinements of this work which include gradient corrections to the LDA, the generalized gradient approximation (GGA), we refer to as P86 (Perdew 1986a,b) and P91 (Perdew 1991). Another functional which incorporates gradient corrections has been derived from an approximate analytic treatment of the helium atom (Colle and Salvetti 1975, Lee *et al* 1988) which we refer to as CS. These functionals have been implemented within the CRYSTAL package as *post hoc* corrections to the HF energy surfaces and are thus based on the converged HF charge density.

The contributions of the HF, empirical dispersion and correlation functionals to the variation of the total energy per unit cell as the Cl–Mg–Cl layers are separated in β-$MgCl_2$ are compared in figure 1. The HF provides a strong repulsion between the layers (figure 1(*a*)) which may be overcome by an empirical dispersion interaction between the anions of the form

$$V_{ij} = \frac{C_6}{|\boldsymbol{r}_i - \boldsymbol{r}_j|^{-6}}. \tag{1}$$

If C_6 is chosen as 75.1 eV Å^{-6}, then the experimental lattice parameter, $c = 5.93$ au, is reproduced (figure 1(*b*)). This value is in keeping with previous estimates of the dispersion interaction between Cl ions (HS1).

Table 1. The energy offsets and predicted c parameters of the various dispersion energy estimates.

Dispersion estimate	PZ	VWN	P86	P91	CS	Empirical
Energy offset (Hartree)	3.5785	1.9455	2.0242	1.9426	1.8903	0.01757
c parameter (Å)	6.56	6.63	< 5.6	5.91	5.90	5.927

The contributions of the correlation functionals are compared to the empirical dispersion in figure 1(*c*). There is an absolute energy offset between the functionals and thus the various contributions have been shifted to an energy zero at the experimental lattice parameter; the offsets are reported in table 1. One does not expect a local density functional to be able to describe the long-range r^{-6} interaction characteristic of dispersion forces and thus discrepancies with the empirical form at large separations are not surprising. In order to predict the correct structure, the first derivative of the energy at the equilibrium lattice constant is required. The gradient-corrected functionals P91 and CS describe the energy gradient remarkably well and thus provide a reasonable estimate of the lattice parameter (table 1). The LDA functionals PZ and VWN yield a very weak interaction between the layers and overestimate the c parameter by approximately 10%. The P86 functional overestimates the interaction and thus overbinds the layers. The tendency of the gradient-corrected functionals to produce accurate lattice properties in materials stabilized by dispersion forces has been noted in parallel studies on graphite and rare-gas solids (Aprà and Causà 1992).

In conclusion, we find that gradient-corrected correlation functionals (CS,P86,P91) may be used to estimate the dispersion-like interaction between the layers in the semi-ionic compound β-$MgCl_2$. The functionals tested do not reproduce the long-range form of the energy surface, as would be expected from their local form, yet

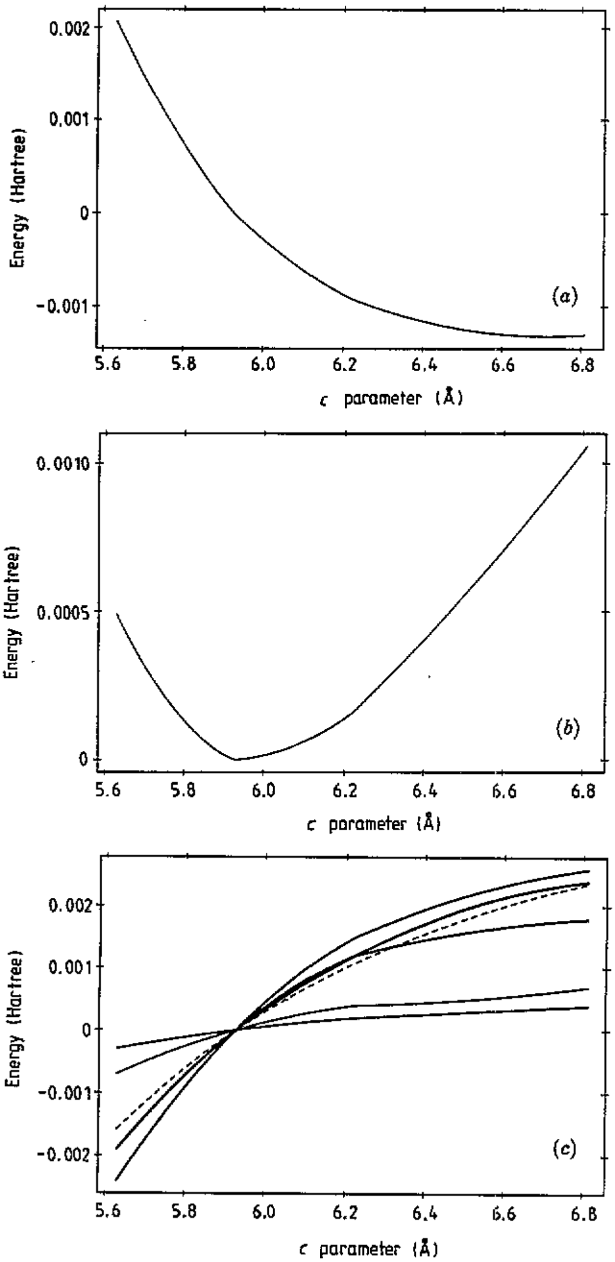

Figure 1. Various contributions to the total energy per unit cell as the Cl–Mg–Cl layers are separated. (*a*) The Hartree–Fock energy. (*b*) An empirical estimate of the dispersion interaction of the anions with $C_6 = 75.1$ eV Å^{-6} is used to correct the Hartree–Fock energy. (*c*) Correlation functional estimates of the dispersion compared to the empirical interaction (dotted line).

a surprisingly accurate description of the static lattice parameters is obtained. The uncorrected LDA description (PZ,VWN) is inadequate in this context.

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