Valence electron correlation energy embracing the diamond-lattice materials C through Sn

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Abstract

By combining a recent result of March and Matthai for the energy gap G with a model of Rey and Savin, the correlation energy e_c of the valence electrons embracing C, Si, Ge and Sn can be estimated. While Sn is thereby predicted to have e_c near to the Ceperley-Alder jellium result corresponding to $G = 0$, diamond exhibits a dramatic reduction in correlation energy due to its large band-gap.

1. Introduction

In recent work in this Journal the ideas underlying insulator-metal transitions has been employed in the diamond lattice semiconductors as Sn is approached via Ge, to construct a three-parameter representation of the energy gap G [1]. The form they found successful was

$$G = A\left(a_c^{1/2} - a^{1/2}\right)^{\gamma} \qquad (1)$$

where a_c = 6.812 Å is the (hypothetical!) value of the mean interelectronic spacing of the valence electrons at which the gap G tends to zero and a is the lattice constant. The exponent γ is found in [1] to be 5/3.

For the diamond lattice semiconductors for which eq. (1) is appropriate, there is by now good evidence that when G is large as in specifically diamond itself, and also in Si to a lesser extent, the local density aproximation (LDA) based on quantal simulations of the jellium model [2] applied to the four valence electrons per atom, does not give quantitative results for the correlation energy.

2. Calculations and result

The availability of the expression (1) has therefore prompted us to revisit a model in which a gap G is introduced into a homogeneous electron gas [3]. These workers have constructed a non-local single-particle potential which allowed the retention of homogeneity in the electron gas, while creating an energy gap G. By adopting this model, they were able to calculate the correlation energy per particle e_c for a homogeneous, spin-compensated, electron

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gas a function of both r_s and G. They also provided an analytic fit to $e_c(r_s,G)$ which is accurate to within a few tenths of a Hartree when compared to their numerical results, This has the form (see also [4]):

$$e_c(r_s,G) = \frac{e_c^{jellium}(r_s) + C_1(r_s)G}{1 + C_2(r_s) + C_3(r_s)G^2}.$$ (2)

Here C_1, C_2 and C_3 are known as analytic functions of r_s [3], while $e_c^{jellium}(r_s)$ is known [2] (note that r_s is proportional to a, where the proportionality constant is dictated by the type of lattice, in the present case the diamond type).

Evidently, by substituting eq. (1) into eq. (2) we have an LDA approximation for the correlation energy per particle embracing the four semiconductors C, Si, Ge and Sn. Fig. 1(a) modifies the plot by Krieger et al. [4] by adding points for these four materials. While Sn is near to what is essentially the Ceperley-Alder result for $G = 0$ (lowest curve in Fig. 1(a)), diamond itself with G large is moved substantially towards the uppermost curve, and the correlation energy/particle E_c is correspondingly reduced.
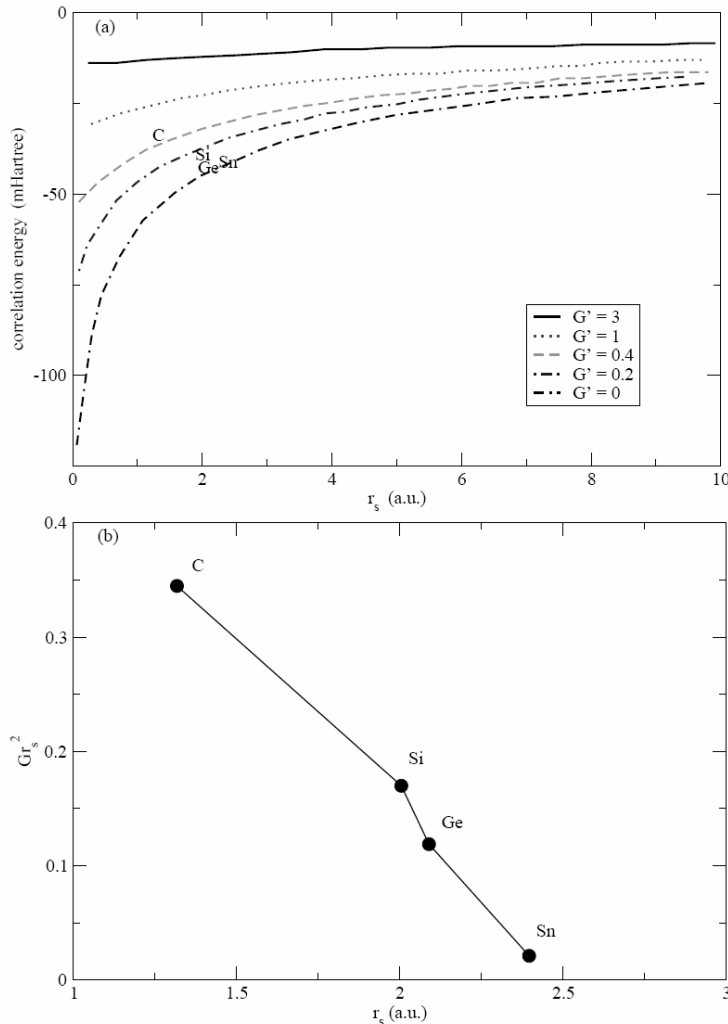

Fig. 1: (a) Correlation energy per particle from Rey-Savin [3] model. Redrawn from Krieger et al. [4], with addition of four points relating to C, Si, Ge and Sn in the diamond structure, Note that the parameter G' in this Figure is the dimensionless gap G/K_F^2 where k_F is the Fermi wave number. (b) Shows $G r_s^2$ versus r_s, with G given by the parametrisation of March and Matthai (see eq. (1)). Note that $G r_s^2$ is proportional to G' in Figure 1(a).

Of course, to use eq. (2) plus (1) for, say, Si, we need knowledge of the density n(r) of the valence-electrons through the unit cell. While n(r) is such that, by expanding in cubic harmonics [5]

$$n(r) = n_0(r) + \frac{xyz}{n^3} n_3(r) + higher orders \qquad (3)$$

the pseudo-valence density has quite substantial angularity for diamond, for Si we can usefully think of small angular deviations around $n_0(r)$. Contours of equidensity n for Si are plotted by way of demonstration in Fig. 2. It is to be noted that the variation of r_s goes from small values on the atomic region to values in the bond region increased by a factor of ≈ 5 for Si.[♥]
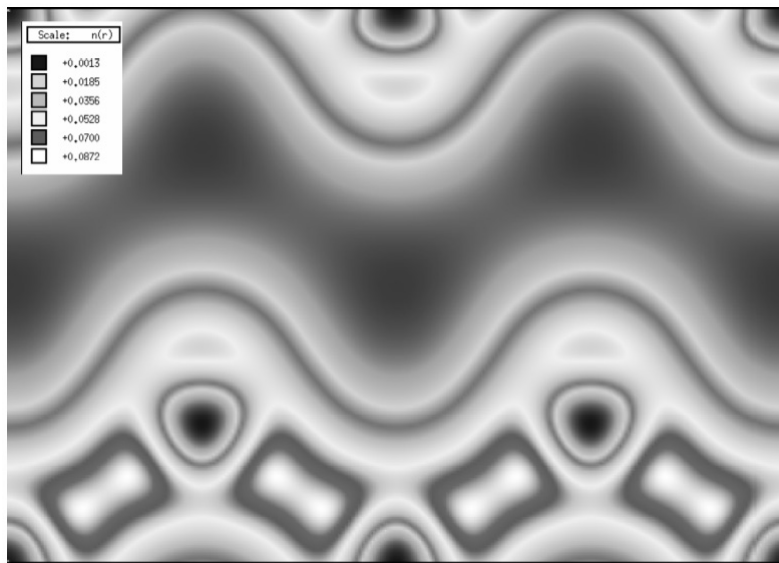

Fig. 2: Valence electron density n(r) for Si in the diamond structure in the (110) plane. Note that using LDA implied by employing eq. (2) for the correlation energy per particle, rs is sampled over a range dictated by the minimum and maximum of the density, 0.0013 and 0.0872 (atomic units), We note that the l=3 symmetry term involving $n_3(r)$ in eq. (2) is relatively more important compared with $n_0(r)$ in diamond itself than in the case of Si plotted in this Figure.

In summary, by putting together the parametric representation (1) for the energy gap *G* in the four diamond-lattice materials C through Sn with the Rey-Savin result (2), a LDA result for the correlation energy/particle is obtained. When combined with eq. (3), the range of r_s needed to be sampled in eq. (2) for Si is proportional to $n(r)^{-1/3}$, where n(r) is plotted in Fig. 2. If we write for the LDA+gap correlation energy per atom in the form

$$\frac{E_c}{N} = \int_\Omega e_c(rn(r))dr, \qquad (4)$$

where n(r) is the valence electron density in the unit cell of volume Ω, then $e_c(r)$ varies more slowly than n(r) and we can usefully write

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[♥]) The first principle calculations are presented in Fgi. 2 were done using DFT in the local-density approximation (LDA) as implemented in the code ABINIT [6]. Core electrons are described by pseudopotentials and the wave-functions are expanded in plane waves with energy cutoff at 24 Hartree for Si.

$$\frac{E_c}{N} = \widetilde{e}_c \int_\Omega n(r)dr = 4\widetilde{e}_c, \tag{5}$$

with 4 valence electrons per atom. From Fig. 1 for diamon $e_c \approx 4$mHartrees and $E_c/N \approx 100$ mH. For Sn, E_c/N remains near to the Ceperley-Alder LDA result.

Acknowledgements

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