

## Electron-correlation energies and the structure of $\text{Si}_{13}$

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A simple physical model for the difference in correlation energies of  $\text{Si}_{13}$  in icosahedral and trigonal prismatic structures yields semiquantitative estimates for this difference, which show that it can stabilize the icosahedral structure relative to the trigonal one by as much as 0.2 eV/electron, or  $\sim 10$  eV per cluster. The same model is compatible with a difference in reactivities between  $\text{Si}_{12}$  and  $\text{Si}_{13}$  of order  $10^3$ , in agreement with experiment.

### I. INTRODUCTION

Elemental clusters  $A_n$  of medium atom number  $10 \lesssim n \lesssim 25$  present interesting challenges for quantum-mechanical many-electron theory. When  $A$  is a nearly-free-electron metal with a weak pseudopotential  $V(q)$ , as for the alkali metals, Mg and Al, theory has been remarkably successful in explaining structural trends in terms of the liquid drop nuclear shell, or jellium model.<sup>1</sup> Recently there has been great interest in the properties of  $\text{Si}_n$ , with special emphasis on  $n=13$ . Other values of  $n$  in the range  $7 \leq n \leq 18$  probably have covalent structures. The latter have been obtained by two different methods, molecular-orbital theory<sup>2</sup> and pseudopotential theory using as basis states plane waves in a box.<sup>3</sup> In the first case<sup>2</sup> electron-electron correlations are treated by low-order perturbation theory<sup>4</sup> on a Hartree-Fock ground state and in the second case<sup>3</sup> by the Slater local-density approximation (LDA) using expressions appropriate to a three-dimensional (3D) free-electron gas with the electron self-interaction energies excluded.<sup>5</sup> These two approaches are quite different, but they obtain remarkably similar results, for instance, with  $n=10$ , so long as the ground-state structure is covalent.

What is special about  $\text{Si}_n$  with  $n=13$ ? Experimentally these clusters are observed<sup>6</sup> to be about  $10^3$  times more stable against chemical reactions with simple molecules ( $\text{C}_2\text{H}_4, \text{O}_2, \text{H}_2\text{O}$ ) than is found for nearby values of  $n$  (11, 12, 15, . . .), and there is an echo of such stabilization again at  $n=19$ . The special numbers  $n=13, 19, \dots$  are familiar from polyhedral geometry as the sums of pentagonal sequences 1-5-1- $\dots$ -5-1, and they correspond at  $n=13$  to the icosahedron and at  $n=19$  to the bi-icosahedron. They were found to be the stable ground states of  $\text{Si}_{13}$  and  $\text{Si}_{19}$  for a classical force field,<sup>7</sup> which accurately reproduces the energies, densities, and compressibilities of the bulk phases of Si, and which includes a back-bonding or surface term designed to reproduce the results of quantum-mechanical calculations<sup>2,3</sup> for small  $\text{Si}_n$  clusters with  $n < 10$ . The calculations preceded the experiments and so may be said to have predicted the experimental anomalies. The parameters of the classical force field were fixed by the bulk phase diagram and the small cluster results and were not modified in any way to

discuss the structures of medium-size clusters.

The puzzle that now arises is that although the quantum-mechanical calculations<sup>3</sup> showed that the ground state of  $\text{Al}_{13}$  was icosahedral, icosahedral  $\text{Si}_{13}$  was found to have an energy 5.3 eV above that of the ground state, a capped trigonal antiprism similar to the ground state of  $\text{Si}_{10}$ . Thus within the usual local-density approximation there is no qualitative difference between the various  $\text{Si}_n$  structures for  $10 \leq n \leq 13$ , and the quantum results disagree not only with the classical model but also with the experimental data<sup>6</sup> as well. The puzzle is the greater considering that the two different quantum methods<sup>2,3</sup> have given such similar results for  $\text{Si}_{10}$ .

In this paper I will argue that the source of this discrepancy lies in an inadequate treatment of electron-electron correlations. It is beyond the scope of this paper to calculate these correlations in detail, but I will present a simple model which shows how these correlations can be much larger for small clusters than for the bulk. With this model the Wigner-Seitz interpolation formula for the correlation energy of a 3D free-electron gas, which was used to calculate the bulk phase diagram for Si and other semiconductors,<sup>8</sup> can be modified to make it suitable for  $\text{Si}_{13}$  in the metallic and covalent structures. This formula shows that the modified correlation energy per electron of the metallic icosahedral structure should be about 0.20 eV larger than that for the covalent trigonal structure as calculated from an unmodified Wigner-Seitz formula. Because  $\text{Si}_{13}$  contains 52 valence electrons this brings the energy of the metallic icosahedral structure below that of the covalent capped trigonal antiprism. The change arises essentially because almost all the atoms of  $\text{Si}_{13}$  are surface atoms. I believe that this example represents the most striking experimental demonstration known of metallic-covalent phase changes in electron-electron correlation energies for medium-size systems of  $\sim 50$  correlated electrons. The simplicity of the two competing structures means that this problem is very well defined and may well reward further computational effort using either the present simplified approximations or more elaborate, more rigorous but also computationally intensive approaches of the quantum Monte Carlo type.<sup>9</sup> Indeed the example of  $\text{Si}_{13}$  may represent the best defined and most demanding challenge that these methods have yet faced.

## II. SURFACE AND BULK CORRELATION ENERGIES

The key to the present model is collective plasma screening of the electron-electron interactions (classical Debye-Huckel or quantum-mechanical Bohn-Pines<sup>10</sup>), which is qualitatively different in  $d=2$  dimensions<sup>11</sup> compared to  $d=3$  dimensions.<sup>10</sup> For the latter the plasma energy  $E_p(q)$  is given by  $\hbar\omega_p + aq^2$  for small  $q$ , with the plasma frequency given by  $\omega_p^2 = 4\pi Ne^2/m$ , where  $N$  is the valence electron density, but for the former  $E_p(q) = bq$  for small  $q$ . There are qualitatively two contributions to the correlation energy,<sup>10</sup> one associated with short-range interactions,  $q/q_c > \beta$ , and one associated with long-range interactions,  $q/q_c < \beta$ . The value of the cutoff  $q_c$  is essentially determined<sup>12</sup> by the point at which  $E_p(q)$  intersects with continuum of pair excitation energies  $\Delta E(\mathbf{k}, \mathbf{k}', \mathbf{q})$  with  $k, k' \leq k_F$  and  $|\mathbf{k} + \mathbf{q}|, |\mathbf{k}' - \mathbf{q}| \geq k_F$ . We measure the electron density by  $r_s$  (in units of the Bohr radius  $a_0$ ), which is 2.0 for bulk Al and Si. The three-dimensional situation for  $r_s = 2.0$  is sketched in Fig. 1(a) for  $d=3$ . Typically  $q_c \sim k_F/2$  for most  $s$ - $p$  metallic or covalent solids.

For  $d=2$  because  $E_p(0)=0$  one has, in effect  $q_c=0$ . This singular situation is not surprising, but it means that great care must be exercised in discussing electron correlation energies in two dimensions. [For example, both the random-phase approximation (RPA) and the Hubbard approximation yield negative values for the pair-correlation function  $g(r)$  as  $r \rightarrow 0$  for  $r_s \gtrsim 1$ .] Probably

the most reliable simple procedure for interpolating between  $d=2$  and  $d=3$  is therefore to interpolate between the  $d=3$  formula for the density-dependent correlation energy of Wigner<sup>10,11</sup>

$${}^3E_c(r_s) = -0.88/(7.8 + r_s) \quad (1)$$

and a similar formula<sup>11</sup> for  $d=2$ ,

$${}^2E_c(r_s) = -1.10/(4.4 + r_s), \quad (2)$$

where the energy unit is Rydbergs. We now discuss how to interpolate between (1) and (2) for medium-size clusters such as  $\text{Si}_{13}$ .

If we examine Fig. 1(a) we notice that  $q_c \rightarrow 0$  as  $E_p(0) \rightarrow 0$ , and it is therefore natural to use  $E_p(0)$  as our interpolation variable. The three-dimensional bulk plasma frequency  $\omega_p$  is determined by the condition

$$\epsilon_1({}^3\omega_p) = 0. \quad (3)$$

For a small metallic sphere the Mie depolarizing fields<sup>13</sup> lead to a different condition

$$\epsilon_1({}^s\omega_p) + 2 = 0. \quad (4)$$

For a free-electron metal,

$$\epsilon_1(\omega) = 1 - \omega^2/\omega_p^2, \quad (5)$$

so that

$${}^s\omega_p^2 = {}^3\omega_p^2/3. \quad (6)$$

This shows that for the metallic sphere collective screening is greatly reduced compared to the bulk metal, and we already can see the need for interpolating between (1) and (2). We do this linearly in the numerators and denominators:

$${}^xE_c(r_s) = N(r_s, x)/D(r_s, x), \quad (7)$$

where

$$N(r_s, x) = -1.0 + 0.22x, \quad (8)$$

$$D(r_s, x) = 4.4 + 3.4x + r_s, \quad (9)$$

$$x = {}^xE_p/{}^3\omega_p. \quad (9)$$

The linear interpretation procedure described by Eqs. (7)–(9) is the natural extension of Wigner's original formula to more complex geometries. Of course, it is provisional and it will be tested against the experimental results for  $\text{Si}_{13}$ . The reader has no doubt already guessed that it works very well.

## III. LOCAL ENERGY GAPS

From a quantum-mechanical viewpoint, a covalent-metallic transition<sup>14</sup> occurs when covalent bonds are formed and there is an energy gap  $\Delta E$  between the occupied valence and unoccupied conduction bands. This is usually described in terms of even (bonding) and odd (antibonding) combinations of atomic orbitals, with a relative reduction  $\Delta\rho$  of the atomic density  $\rho$  in the covalent phase  $\Delta\rho/\rho \sim -0.2$ , in other words the phase transition

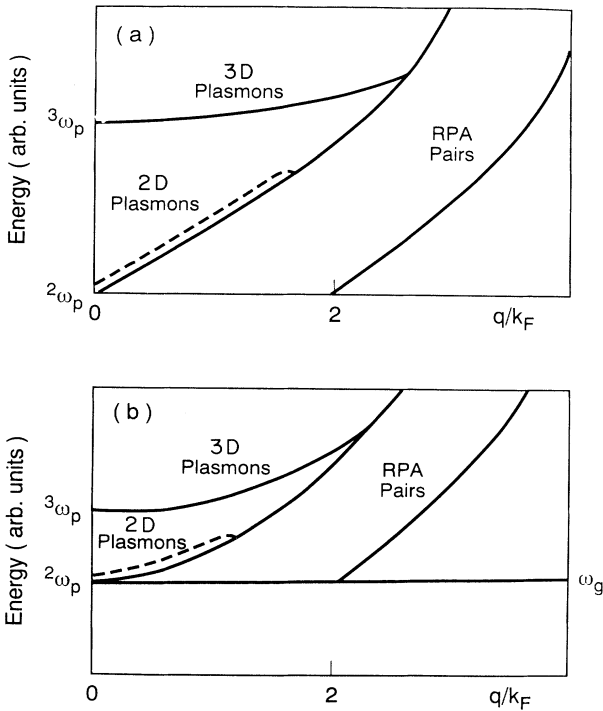


FIG. 1. Pair excitation regions of a nearly-free-electron gas, and plasmon dispersion in three (solid) and two (dashed curve) dimensions, respectively, for (a) the case  $\omega_g = 0$ , free-electron gas, and (b)  $\omega_g > 0$ , isotropic energy gap in a nearly-free-electron gas.

is strongly first order. A surprising aspect of the structure of medium-size  $\text{Si}_n$  clusters is that as a function of the strength  $\gamma$  of the back-bonding parameter the ground configurations of these clusters also collapse abruptly at  $\gamma = \gamma_c$  (as measured by average coordination number) as that force is increased.<sup>15</sup> In other words, the quantum-mechanical compressive effect of increased electron-electron correlation energies in medium-size clusters compared to the bulk crystal clearly produces first-order “phase transitions” in such clusters when it is represented by this classical force-field parameter. The calculations show that  $\gamma_c$  varies slowly with  $n$  in general, as one would expect, except at  $n = 13, 19,$  and  $23$ . Our task now is to find a quantitative way of incorporating the covalent-metallic transition into the Wigner-Jonson-Srinivasan interpolated interpolation formulas, Eqs. (7)–(9).

Again this appears to be a difficult problem, but there is a simple heuristic solution based on introducing an average energy gap  $E_g = \hbar\omega_g$  between the valence and conduction bands.<sup>16</sup> The average gap is derived from the bulk electronic polarizability  $\epsilon_1(\omega)$  without local-field correlations (RPA) in the limit  $\omega \rightarrow 0$ , but it is valid over a wide range of energies. For example, it fits the values of  $\epsilon_2^{-1}(\omega_p)$  for cubic C, Si, Ge, GaP, and GaAs, as measured by electron-energy-loss spectroscopy, within a few per cent.<sup>17</sup> As  $\omega_g$  increases, the correlation energy  $E_c$  is reduced. Little is known about  $E_c(r_s, \omega_g/\omega_p)$  and even that is based on the RPA, which breaks down<sup>11</sup> anyway for  $d=2$ . However, this question can be examined very simply in total-energy calculations<sup>3,8</sup> if we further interpolate not only on  $r_s$  but also on  $\omega_g$ . This will have little effect on the phase diagram<sup>8</sup> of bulk Si, but it may be much more important to understanding the effects of back-bonding of surface atoms on the structure of  $\text{Si}_{13}$ . Many natural interpolation formulas implicitly decouple competing dynamical effects (exchange, plasmon screening, local fields) in an RPA-like way, and optimize each interaction separately. When this is done for large  $r_s$  the pair-correlation function  $P(0, \mathbf{r})$  can become negative in  $d=3$  dimensions<sup>18</sup> and the problem is even more serious<sup>11</sup> for  $d=2$ . A negative value of  $P(0, 0)$  makes the effective interaction energy attractive at small  $r$ , and when the physical condition  $P(0, \mathbf{r}) \geq 0$  for all  $r$  is imposed, the effective interaction is always repulsive and  $E_c$  is reduced. We can avoid this problem with regard to local fields or covalent bonding as described by  $\omega_g$  by assuming that orbital one-electron correlation energies as measured by  $\omega_g$  are partially complementary with plasma screening. As shown in Fig. 1(b), for  $d=2$  we have  ${}^x\omega_p \rightarrow \omega_g$  so that increasing  $\omega_g$  has the effect of increasing  ${}^x\omega_p$  for larger  $q$  values. This in turn reduces the additional correlation energy represented by  ${}^2E_c(r_s) - {}^3E_c(r_s)$ . Thus for  $\omega_g > 0$  we renormalize for  $d=2$  the value of  ${}^x\omega_p$  used in Eq. (9) so that it is given by

$${}^x\Omega_p^n = {}^x\omega_p^n + \omega_g^n, \quad (10)$$

with  $n=1$  and for small clusters where almost all the atoms are surface atoms,

TABLE I. Parameters used for estimating the correlation energies  $E_c(\text{Si}_{13})$  for covalent and metallic isomers of  $\text{Si}_{13}$ . Here  $r_s$  is measured in units of Bohr radius  $a_0$  and all the energies, including  $E_c$  are in eV.

System	$r_s$	$\hbar\omega_p$	$E_g$	$\hbar\Omega_p$	$x$	$E_c$
${}^3\text{Si}$ (cov)	2.00	16.6	4.5	16.6	1.0	
${}^3\text{Si}$ (met)	1.88	16.6	0	16.6	1.0	
${}^2\text{Si}$ (cov)	2.00	0	4.5	4.5	0.27	
${}^2\text{Si}$ (met)	1.88	0	0	0	0.0	
${}^3\text{Si}_{13}$ (cov)	2.00	9.6	5.0	14.6	0.88	-1.32
${}^8\text{Si}_{13}$ (met)	1.88	9.6	0	9.6	0.58	-1.61

$$x = {}^x\Omega_p / {}^3\omega_p. \quad (11)$$

Note that an RPA-like renormalization in (10) would use  $n=2$ . Admittedly the use of  $n=1$  is heuristic, but Wigner used linear interpolation on  $r_s$  between the high-density electron gas ( $r_s < 1$ ) and the low-density electron crystal ( $r_s > 10$ ) and obtained remarkably accurate results for metallic densities ( $2 \lesssim r_s \lesssim 5$ ). Similarly I hope that the linear interpolation on frequency in (10) will succeed equally well for small cluster correlation energies. It describes  ${}^x\Omega_p$  correctly in the two-dimensional limit  ${}^x\omega_p \rightarrow 0$ ,  ${}^x\Omega_p \rightarrow \omega_g$  [see Fig. 1(b)] and may continue to be valid so long as  ${}^x\Omega_p \lesssim {}^3\omega_p/2$ .

The values of  ${}^3\omega_p$  and  $\omega_g$  that determine  ${}^x\omega_p$  and  ${}^x\Omega_p$ , together with  $r_s$ , are listed in various cases in Table I. The energies, including  $E_c$ , are in eV. In the lower right corner of the table are the estimated energy differences between  $\text{Si}_{13}$  in the covalent trigonal prismatic and metallic icosahedral structures. Using only  ${}^3E_c$  to estimate this difference, as was done in the LDA calculations, makes these two energies equal to within 0.05 eV. The present model, which recognizes the breakdown of the RPA for  $d=2$  and uses an interpolation between  $d=2$  and  $d=3$  to estimate this difference, increases the correlation energy contribution to this difference by 0.3 eV. The previously calculated difference in total energy between the two structures<sup>3</sup> was only 0.1 eV. Thus it appears that a modification of the correlation energy in the present manner is more than adequate to stabilize the icosahedral structure.

#### IV. CHEMICAL REACTIVITIES

It may be, as suggested earlier,<sup>7</sup> that the difference in structure alone between the covalent and metallic phases explains the thousandfold reduction in chemical reactivity of  $\text{Si}_{13}$  compared to  $\text{Si}_n$  for  $n$  near 13. However, more generally one expects the metallic structure to be more reactive than the covalent structure just because the former is more polarizable than the latter (it has a smaller energy gap). Thus the difference in reactivities seems to be in the opposite direction from one's expectations.

The resolution to this problem lies in recognizing that the chemical reactivities depend not on the average gap  $E_g$ , which was used above to discuss correlation energies, but rather on the states nearest the Fermi energy, which

chemists refer to as the highest occupied and lowest unoccupied molecular orbitals. This would usually be described by physicists as the anisotropy of the energy gap, which means that the smallest energy gap  $\Delta E_{\min}$  is generally much smaller than the average gap  $E_g$ . (In bulk Si,  $\Delta E_{\min} = 1.1$  eV and  $E_g = 4.5$  eV, for example.) In very isotropic systems one can have  $\Delta E_{\min}$  almost the same as  $E_g$ . (This is the case in *a*-Si, for instance.<sup>19</sup>) Thus we expect that even though  $E_g$  (metallic, icosahedral Si<sub>13</sub>)  $\ll E_g$  (covalent, trigonal Si<sub>13</sub>), one can still have  $\Delta E_{\min}$  (covalent, trigonal Si<sub>13</sub>)  $\ll \Delta E_{\min}$  (metallic, icosahedral Si<sub>13</sub>). If  $\Delta E_{\min} \approx E_g$  (metallic Si<sub>13</sub>)  $\sim 1.5$  eV and  $E_g$  (covalent Si<sub>13</sub>)  $\sim 4.5$  eV then we would still have, according to the above analysis, a difference of correlation energies  $\sim 0.2$  eV (instead of 0.3 eV), which is sufficient to reverse the energy difference of  $\sim 0.1$  eV favoring the trigonal structure.<sup>3</sup> At the same time, if the effective quenching temperature in the molecular beam which determines the relative isomer populations is  $T_q \sim 2 \times 10^3$  K, then a 1.0-eV difference in  $\Delta E_{\min}$  would stabilize metallic Si<sub>13</sub> relative to covalent Si<sub>12</sub> by a factor of  $e^{20} \sim 10^6$ , which is again more than adequate. In short, we see that with reasonable numerical estimates, all consistent with well-known qualitative trends, we can explain the central features observed experimentally.

## V. CONCLUSIONS

The calculation of electronic correlations energies  $E_c$  in systems like Si<sub>*n*</sub> clusters ( $10 < n < 20$ ) is an extremely formidable problem which at present is still unsolved. The purpose of this paper is modest: it attempts to argue, from a physical model, that because nearly all the atoms of such clusters lie on the cluster surface, that to a first approximation the correlation energy should be estimated from interpolation formulas for  $d = 2$  and  $d = 3$  that interpolate between the high-density ( $r_x \lesssim 1$ ) gas and low-density ( $r_x \gtrsim 10$ ) electronic crystals. The dimensional interpolation in turn is based on classical local-field or depolarization effects for small spheres. This model is admittedly simplistic, but it is unambiguous and it provides a basis for making a first estimate for such correlation energies. It shows that the usual approach, which relies entirely on the  $d = 3$  correlation energy, may considerably underestimate  $\Delta E_c = |E_c(\text{icosahedral Si}_{13}) - E_c(\text{trigonal Si}_{13})|$ . It thus provides a plausible basis for understanding the very large factors ( $\sim 10^3$ ) which differentiate the reactivities<sup>6</sup> of covalent Si<sub>12</sub> and Si<sub>15</sub> from Si<sub>13</sub>. It may be hoped that this model, in spite of its shortcomings, will stimulate further theoretical interest in this dramatic and well-defined problem.

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