Predicting New Solids and their Properties [and Discussion]

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Predicting new solids and their properties

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It is now possible to predict properties of materials using quantum theory and minimal information about the constituent atoms of a solid. Accurate calculations explaining and, in some cases, predicting electronic, structural, vibrational, and even superconducting properties of solids have been performed. Here we provide an overview of this area with emphasis on the predictive capacity of the approach. A few of the applications which will be highlighted include the analysis of high-pressure structures of solid, compounds having very low compressibilities, and metallic hydrogen.

1. Introduction

The theory of bonding and structure of solids has evolved considerably in the past 30 years. The quantum theory developed in the 1920s provided the fundamental tool for exploring solids, but the invention of appropriate models and the mechanics for solving the resulting differential equations were required before applications to real systems could be made. At first, considerable physical insight was achieved with simple models. Later, the advent of high-speed computers allowed the use of more appropriate complex models. Today computer modelling of materials is a successful industry and interesting advances are being made at a rapid rate (Cohen 1986). An early worry that computer modelling would lead to mindless exercises or crank-turning without physical understanding is rarely stated nowadays. Mindless calculations can be done without a computer and most researchers feel that the use of modern computational equipment allows boarder exploration of physical phenomena by reducing some of the constraints arising from mathematical and physical complexity. As a result we are in the fortunate situation for many subareas of condensed matter physics where theorists can contribute more effectively in the three conventional modes expected of them. Firstly, there is the task of explaining specific observed phenomena. Secondly, the development of concepts, arguments, or robust theories to bring together the results of a variety of experiments with unifying principles. Finally, there is prediction. The use of theory to predict new results is particularly challenging in the field of condensed matter physics where few predictions are ignored by able experimentalists. In practice it is not unusual to find theorists working in two or three modes at once.

The evolution of the theory of bonding and structural properties of solids is a particularly good example of the metamorphosis which has taken place more generally in condensed matter theory. It is also an area where successful predictions are being made. After a brief description of some of the approaches and models used,

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a few applications will be described as examples to illustrate the successes of the models and concepts and to indicate some future directions of this field.

2. Models

Because of the successes in the application of quantum theory to understand the properties of atomic and molecular systems, it was natural to view clusters of atoms and solids as weakly perturbed collections of atoms or molecules. This approach has been used successfully by quantum chemists and physicists for systems in which the bonding between the atoms or molecules does not significantly perturb their electronic energy levels. For most metals and semiconductors, the opposite is true. In fact, it is usually a better starting point is to consider free electrons weakly perturbed by the ionic potential. The unperturbed free electron model was used by Sommerfeld and others to explain many properties of metals (Kittel 1986). When this model is used, the Fermi statistics and spatial constraints on the electron gas manifest themselves in most of the physical properties particularly at low temperatures. To go beyond the simplest free-electron model which considers only the kinetic energy contribution, it is convenient to use a jellium model where the electrons move freely in a structureless positive jelly arising from a smeared out distribution representing the ions. The total electronic energy E_e (in rydbergs) of the system is composed of kinetic, exchange, and correlation energies, and all are functions of the electron gas parameter r_s,

$$E_e = 2.2099/r_s^2 - 0.9163/r_s - 0.094 + 0.0622 \ln r_s. \tag{1}$$

The above expression is accurate as $r_s < 0$ and for large solids where surface effects can be neglected. Even though $2 < r_s < 5$ for most metals, this is still a good starting point for bulk solids and with some refinements surface effects can be explored for finite samples.

A recent success of this model is its application to metal clusters. Jellium spheres and ellipsoids have been used to stimulate clusters of alkali atoms (de Heer *et al.* 1987). The confinement of the electrons in the jellium spheres and ellipsoids leads to electronic energy levels and shell structure which in turn are responsible for the stability of clusters with specific or 'magic' numbers of atoms. The self-consistent potential for the electrons resembles that of the intermediate well in figure 1 which gives magic numbers at 2, 8, 18, 20, 43, 40, ... This electronic shell structure is basic to the theory and the resulting calculations of the abundance spectra, ionization potentials and many other electronic properties of metal clusters are generally in agreement with the measured results. Because the jellium model is used, the structural arrangement of the atoms does not play a role in this approach. Calculations (Cleland & Cohen 1985) based on pseudopotentials for specific structural arrangements of atoms yield results which are consistent with the jellium spectra. Hence the crystal field effects do not significantly alter the shell structure.

When large clusters are formed (Göhlich *et al.* 1990) the transition to the bulk can be studied. For free-electron-like metals, small bonding features in the electron density appear when the cluster size is sufficiently large. A nearly-free-electron model with the electron–ion potential treated in perturbation theory can be used to describe this behaviour. A similar approach can be applied to semiconductors and even some insulators. The electron–ion potential can be approximated using a pseudopotential approach (Heine 1970; Cohen & Heine 1970) where the core electrons are assumed to

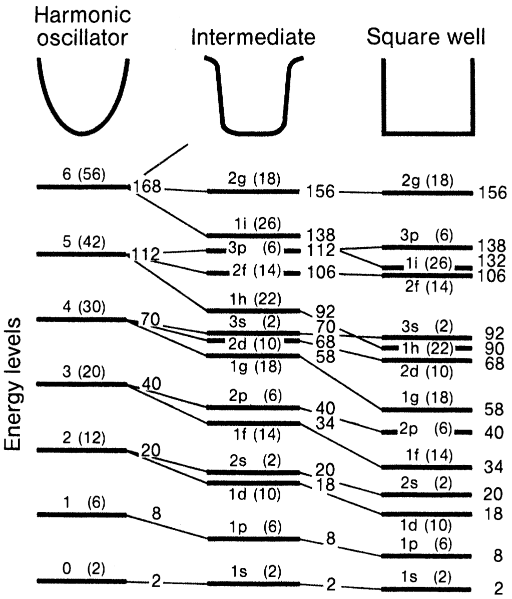

Figure 1. A comparison of the energy level spectrum for a three-dimensional harmonic oscillator (left), a square-well potential (right), and a potential intermediate between these two. The numbers inside the rectangles refer to energy level labels while those in parenthesis refer to degeneracies. The numbers outside the rectangles give the cumulative number of states. The intermediate case is representative of that found for simple metal clusters.

be unchanged in going from the nearly isolated atoms state appropriate for a gas of atoms to the strongly interacting atoms state of a solid. Now the total energy of the system includes the electronic energy, the energy of the ionic cores and the electron–core interaction energy. For rigid cores, the total energy is

$$E_{\text{total}} = E_{\text{ke}} + E_{\text{e-c}} + E_{\text{e-e}} + E_{\text{c-c}}, \tag{2}$$

where E_{ke} is the electron kinetic energy; $E_{\text{e-c}}$, $E_{\text{e-e}}$, and $E_{\text{c-c}}$ are the electron–core, electron–electron and core–core contributions to the energy.

The pseudopotentials needed to represent the electron–core interactions can be extracted from experimental data (Cohen & Chelikowsky 1988) or generated (Starkloff & Joannopoulos 1977; Zunger & Cohen 1979; Hamann *et al.* 1979; Kerker 1980; Louie *et al.* 1982) from atomic wavefunctions. The former approach is the empirical pseudopotential method (EPM) while the latter is often called the '*ab initio* or first principles' pseudopotential approach. The EPM generally starts with optical data and yields an interpretation of the data together with pictorial representation of the electronic charge density, the band structure, dielectric functions, densities of states, etc. Calculations in the 1960s and 1970s using the EPM gave rise to predictions of band structures which were later shown to be correct using angular resolved photoemission. These studies also introduced electron density plots and successfully predicted the bonding distribution of the electrons.

Since the EPM uses potentials derived for the bulk solid it is not appropriate for calculations which involve the rearrangement of charge such as occurs at surfaces, near defects, or as a result of solid–solid structural phase transitions. For these cases the core pseudopotentials are used together with a model for the electron–electron

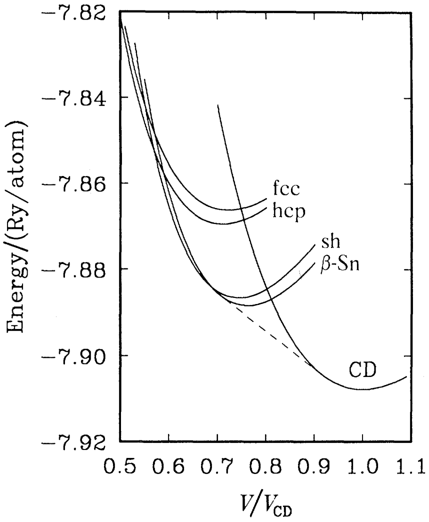

Figure 2. Calculated total energy as a function of volume for Si in the cubic diamond, β-Sn, simple hexagonal, hexagonal-close packed, and face-centred-cubic structures. The volume is normalized to the calculated volume for cubic diamond (V_{CD}).

interaction energy. A phenomenological approach to estimate the electron–electron potential can be used based on Slater's (1951)X–α model, or a more first principles scheme such as the local density approximation (LDA) (Kohn & Sham 1965) can be applied. The latter scheme is appropriate for calculating ground-state energies; it is particularly useful for determining structural and vibrational properties of solids. These properties can be computed (Cohen 1982) by considering the total energies of model systems for different structural arrangements. An example for Si is given in figure 2. This approach has had wide application for determining crystal structures at high pressures and mechanical properties such as compressibility. For vibrational properties, the atoms are moved to simulate a phonon distortion and then total energies or forces are computed to give phonon frequencies and related properties such as electron–phonon interactions.

Hence the use of pseudopotentials and the LDA allows broad studies of ground state properties of solids. Excited state properties such as those important for explaining optical processes require more complex schemes. A quasi-particle approach (Hybertsen & Louie 1986) for dealing with excited states relies on the calculation of the electron self-energy and local field effects. This method has been applied to several systems with success. Semiconductor and insulator band gaps which are underestimated using the LDA are found to be in good agreement with experiment when the quasi-particle spectrum is calculated using the above scheme. Furthermore, improvements for ground-state properties are found when electronic correlation effects are computed using quantum Monte-Carlo methods (Fahy *et al.* 1988).

Since the total energy approach usually relies on the comparison of energies for competing candidate structures or structural configurations (as shown in figure 2), it is limited by the choice of the candidates examined. Educated guesses and experimental data can be used to narrow the number of choices. If forces on the atoms in a specific structure are evaluated it is sometimes possible to determine the directions in which to move the atoms to obtain a minimum energy structure. This is particularly useful for surface structures where the number of possible distortions are more limited. A more promising approach (Car & Parrinello 1985) is to use Monte-Carlo sampling techniques for atoms moving randomly. Energy minimization procedures based on molecular dynamics schemes are developing at a rapid pace and it should be possible to explore a wide range of parameter space in the future.

3. Applications

As discussed previously, the EPM has a long list of applications (Cohen & Chelikowsky 1988) to electronic structure and optical properties. Its accuracy is rivalled only by the first-principles quasi-particle calculations (Hybertsen & Louie 1986). Since the EPM is much simpler it has had broader applications, but it requires experimental input. For ground-state properties, the total energy pseudopotential–LDA approach (Cohen 1982) has been applied most extensively. One impressive result is the successful prediction of hexagonal phases of Si, their structural properties, and the existence of superconductivity in these covalent metals systems (Chang *et al.* 1985). Other high-pressure phases have been predicted and their properties explained. It is gratifying that this first-principles approach which uses only the atomic number and atomic mass as input is capable of giving ground-state structural properties such as lattice constants, bulk moduli, the Poisson ratio, etc., with high precision. In addition vibration properties such as phonon spectra, Gruneisen constants, and the characteristic properties of solid-state structural transitions such as transition pressures and transition volumes are computed accurately.

Below two recent applications are discussed in some detail. These are the search for low compressibility or very hard solids and the properties of solid hydrogen at high pressures.

(*a*) *Low compressibility solids*

At present the largest bulk modulus and hardest known substance is diamond. Although hardness can be influenced by macroscopic defects, for ideal crystals, the bulk modulus is the best indicator of hardness. Since the bulk modulus depends on the microscopic bonding of the solid, it can be calculated from first principles. One direct approach for calculating the bulk modulus is by using the total pseudopotential method to compute the dependence of the energy on volume. Using a Murnahan (1944) or Birch (1952) equation of state to fit the calculated curves, the bulk modulus and its pressure derivative can be obtained. Although this approach works well, it requires considerable computer time. A simpler but empirical scaling approach is described below. This method allows the investigation of material trends and provides simple formulae for estimating bulk moduli.

The scaling approach (Cohen 1985) is based on the following observations. For a free electron system the bulk modulus

$$B = \tfrac{2}{3}nE_{\mathrm{F}}, \tag{3}$$

where n is the electron concentration and E_{F} is the Fermi energy. Equation (3) can be interpreted as a scaling relation for B in which the bulk modulus scales like the bonding energy divided by the bond volume. The extension to covalent semiconductors is based on the spectral model developed by Phillips and Van Vechten

(Phillips 1984). In this model the average optical gap E_g is assumed to have a homopolar contribution E_h and an ionic contribution C, where

$$E_g^2 = E_h^2 + C^2. \tag{4}$$

The values of E_g, E_h and C can be extracted from experiment and their dependence on bond length can be determined (Phillips 1984).

In a series such as the Ge, GaAs, ZnSe row of the periodic table, E_h and the lattice constant remain unchanged. It is the ionic contribution C which changes the average gap which appears in the optical spectrum. The covalent nature of the bond determines the bond length and is the major factor in determining the size of the bulk modulus. If the bond is taken to be cylindrical with a radius of order the Bohr radius and a length d, then the scaling of B discussed in relation to equation (3) suggests that

$$B = 45.6\, E_h\, d^{-1}, \tag{5}$$

where E_h (in electronvolts) is considered to be the bond energy and B is given in GPa when d is in ångströms†. Since E_h scales as $d^{-2.5}$, a relation which depends only on d can be derived

$$B = 1761\, d^{-3.5}. \tag{6}$$

In the above discussion the ionic factor is ignored. A simple extension to include ionicity can be made by introducing a parameter $\lambda = 0, 1, 2$ for group IV, III–V and II–VI materials. The resulting equation

$$B = \tfrac{1}{4}N_c\,(1971 - 220\,\lambda)\, d^{-3.5} \tag{7}$$

gives agreement within a few percent of the measured values of the bulk modulus of valence 8 compounds where $N_c = 4$. A generalization to non-octet compounds which do not have complete tetrahedral bonding can be made if one considers the density of the bonds in addition to the strength of the bonds. Defining N_c as the average coordination number in the crystal, then the factor $\tfrac{1}{4}N_c$ multiplies the result in equation (7).

As is evident from (7), the bulk modulus increases as d and λ decrease. Although diamond sets the limit at present there is no *a priori* reason to expect that the value $B = 443$ GPa for diamond is an upper limit. In particular it was suggested (Cohen 1985) that compounds based on carbon and nitrogen might exhibit values of B comparable with that of diamond. The C–N bond length is short and this bond is not very ionic. The empirical scaling approach does not predict d, however, if atomic radii are used to estimate d, the expected values of B are very large, Unfortunately, complete tetrahedral coordination is not expected since a zincblende structure with an occupied antibonding band does not appear favourable.

To test the viability of having a C–N compound with a very high B, the first-principles total energy approach was used (Liu & Cohen 1989). This method requires a candidate crystal structure. The structure chosen is the β-Si_3N_4 structure (figure 3) which is known to exist. Assuming this structure, the ground-state properties of β-C_3N_4 are computed using the pseudopotential total-energy approach within a localized-orbital formalism (Chelikowsky & Louie 1984). The hexagonal unit cell chosen contains two formula units and the structure can be viewed as a C–N network with sp^3 hybrids on the C atoms and sp^2 hybrids on the N atoms. This three-dimensional network is rigid and is a good prototype for achieving a low compressible form of C–N even though the bonding is not completely sp^3.

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† 1 Å = 10^{-10} m.

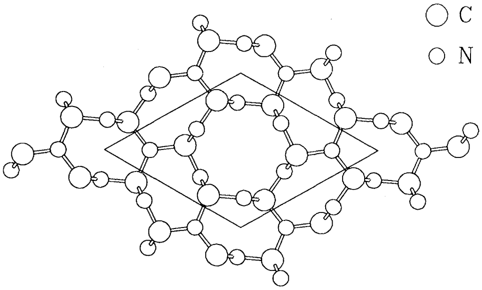

Figure 3. Structure of β-C_3N_4 in the *a*–*b* plane. The *c*-axis is normal to the page. Half of the atoms illustrated are located in the $z = -\frac{1}{4}c$ plane and the other half are in the $z = \frac{1}{4}c$ plane. The parallelogram indicates the unit cell.

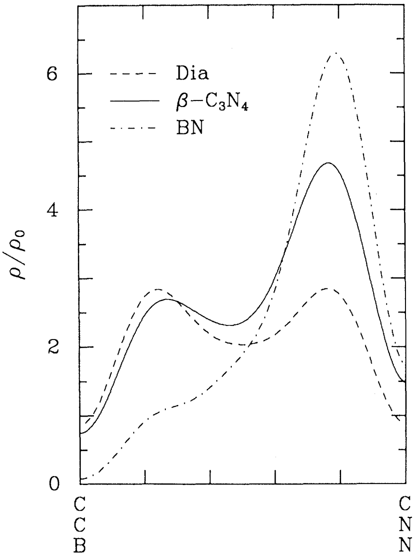

Figure 4. Comparison of the normalized valence charge density along the bond for diamond, β-C_3N_4 and BN. The normalization factor for the charge density, ρ_0, is the number of valence electrons per cell.

The calculated total energy against volume for β-C_3N_4 yields a C–N bond length of 1.47Å which is intermediate between the sum of the C tetrahedral and N sp^2 radii and the sum of C and N tetrahedral radii. At the equilibrium volume, the cohesive energy is 81 eV per cell or an average of 5.8 eV per atom which suggests that this structure has a reasonable chance of being metastable. The bulk modulus is calculated to be 427 ± 15 GPa which is comparable to the value of 443 GPa for diamond. Using the calculated mass density and bulk modulus, the average bulk velocity of sound is estimated to be 1.1×10^6 cm s^{-1}. The electronic charge density along the C–N bond is similar to that of a C–C bond in diamond except for some excess charge on the N site. A comparison with diamond and BN is given in figure 4.

The prototype β-C_3N_4 calculation demonstrates that solids based on C and N can be metastable and if formed should have very large bulk moduli. In addition, the good agreement between the estimates of the bulk modulus from equation (7) and from the total energy calculation adds support for the use of the scaling formula to investigate trends. It is hoped that experiments using high temperatures, high pressures, molecular beam epitaxy or plasma deposition will lead to the fabrication of β-C_3N_4 or similar phases. Although detailed calculations were not done for α-C_3N_4 (C–N in the α-Si_3N_4) structure, this structure should also be a favourable candidate. Amorphous phases of C_3N_4 are also of considerable interest. In addition to their low compressibility, the wide band gaps and high thermal conductivities expected for C–N compound make these materials interesting from a technological as well as a scientific point of view.

(b) *Metallic hydrogen*

Although solid hydrogen is an insulator at low temperatures and pressures, there is great interest in exploring higher-pressure solid phases which are likely to be metallic. Wigner & Huntington (1935) suggested that at high pressures the H_2 molecular bond would be broken and a monatomic metallic system would result. Another possibility for a metallization is an insulator–metal transition caused by band overlap. The resulting molecular metal would still have strong short H_2 bonds with longer bonds linking the dimers. Theoretical estimates of the pressure for the transition to an atomic metal are in the range of 3–5 mbar† (Min *et al*. 1986; Ceperly & Alder 1987; Barbee *et al*. 1989*a*). Estimates of the transition pressure to a molecular metal phase are at much lower values in the range of 2 mbar (Min *et al*. 1986; Barbee *et al*. 1989*a*; Ramaker *et al*. 1975; Friedli & Ashcroft 1977). These calculations are not definitive because the structural phases of the high-pressure insulator and metallic phases are not known.

Recently theoretical activity in this area has intensified because of the interpretation of some experimental data as evidence of metallization (Mao & Hemley 1989; Eggert *et al*. 1990). Several experimental studies in the range of 150 GPA suggest there is a transition to a new phase, hydrogen-A (H-A). The measurements indicate that below the transition the structure is hcp and continuity of the Raman active phonon mode suggests that the H-A phase is also hcp, but there is a discontinuous change in the frequency of the vibron mode near the transition. Some optical data (Mao *et al*. 1990) suggest free carriers and Drude behaviour.

To investigate the possibility of band overlap around 150 GPa, an LDA calculation was modified using an X–α potential (Garcia *et al*. 1990). The band structure calculation is done for an oriented arrangement of the molecular axes and for a disordered phase modelled by a structure factor which produces spherically symmetric charge distributions. Using experimental input for structural properties and the zero pressure band gap, the density dependence of the minimum indirect gap is determined for the oriented and spherically symmetric phases. As shown in figure 5 band overlap occurs at a much higher density for the latter phase. When the experimental equation of state is used, the calculated critical densities lead to estimates of 180 ± 20 GPa and 400 ± 40 GPa for the transition pressures giving band overlap for the oriented and spherically symmetric phases, respectively.

Although the LDA calculations significantly underestimate the transition pressures as expected, the ordering found in the X–α calculation is the same. Previous comparisons between LDA, X–α, and quasi-particle calculations indicate that LDA estimates are low while X–α estimates are a bit high compared with quasi-particle calculations for the density corresponding to a zero gap transition. Recently (Chacham & Louie 1991) have completed a first-principles quasi-particle study of the oriented phase and estimate that overlap occurs at 150 GPa.

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† 1 bar = 10^5 Pa.

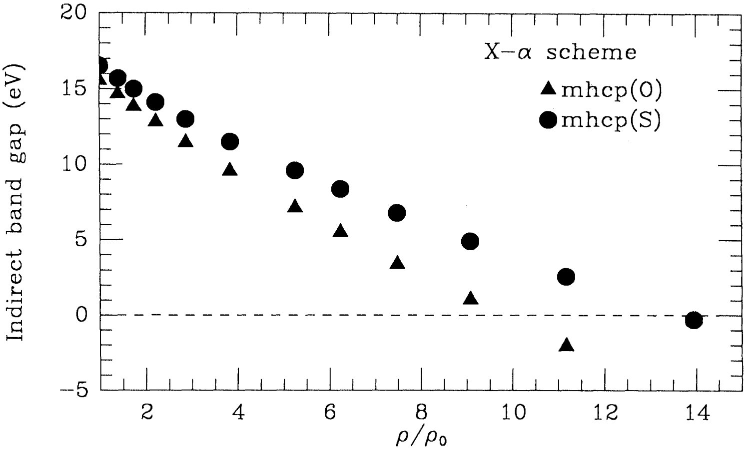

Figure 5. Indirect band gap against density for molecular-hexagonal-close-packed hydrogen assuming oriented molecules (triangles) and spherically symmetric molecules (solid circles). The calculation was done using the Slater X–α exchange potential.

The transition to the monatomic metallic phase can be studied by examining a variety of structural candidates and comparing their enthalpies as a function of pressure. It was shown (Barbee *et al.* 1989*a*) that the primitive hexagonal (PH) phase is favoured relative to several other common structures. However, when the phonon spectra was calculated (Barbee *et al.* 1989*b*) imaginary harmonic phonon frequencies were found indicating that a transition to another structure is favoured. By tripling the unit cell along the hexagonal *c* axis a lowering of the energy was found. Although this distorted hexagonal structure has a low energy, some phonon modes appear to be unstable signalling yet another transition. An interesting low-energy structure is the 9*R* structure found in Li at low temperatures; calculations based on this structure are in progress.

By calculating the phonon spectra for various low-energy structures and electron–phonon matrix elements, estimates of the electron–phonon parameter $\lambda \approx 1$ are made. Although this is a moderately large value of λ, the presence of high-energy phonons arising from the low hydrogen mass leads to estimates of superconducting transition temperatures T_c in the range of 100–200 K. The value of T_c depends on crystal structure and the resulting electronic properties. Because of similarly expected high phonon frequencies in the molecular metal, if the electron–phonon matrix elements are comparable with those found for the monatomic metal, then T_c should also be large for this system.

4. Conclusions

The emphasis here is on the robustness of the pseudopotential total energy approach. Its evolution from the nearly-free-electron gas model and the development of refinements to the model have provided a useful tool and significant physical insight into the behaviour of solids and clusters. There have been dozens of applications; only a few are highlighted here. Possible future paths including taking advantage of the developments in calculating excited states, correlation energies, and molecular dynamics schemes. Once these approaches are refined and simplified, it should be possible to use one computational approach to compute ground-state and excited-state properties for previously observed or new hypothetical systems obtained by Monte-Carlo type searches.

If the above goals are achieved it is likely that they will lead to even more ambitious undertakings. However, regardless of future advances, it is encouraging to note that even now successful predictions are being made of new materials and new properties. And as described earlier, when the methods are pushed to their present limits, there are the suggestions of materials with hardness comparable with diamond and a superconductor with a transition temperature above any found thus far.

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Discussion

Z. Reut (*City University, London, U.K.*). The discriminating ability of the pseudo-potential should be quantified; i.e. what are changes in the pseudo-potential when going from lighter to heavier elements, up and down in the Mendeleev periodic system of elements? This is related to the effectiveness of the predictive methods.

M. L. Cohen. There are some standard variations which are quite interesting; these are well described by the pseudopotential approach. As an example, let me choose column IV of the periodic table. For carbon, there are no p states in the core and as a consequence no repulsive p core pseudopotential. The valance p electrons lie close to their atomic spatial positions in C whereas for Si they are pushed out toward the centre of the Si–Si bond. The absence of d core states for Si has similar effects on the d valence electrons and the metallic component of the bonding which increases as one moves to Sn and Pb. Upon reaching the Pb row, relativistic effects become more important and the s and p states move apart in energy making it more difficult to construct sp^3 orbitals. The pseudopotential calculations of material properties illustrate these trends. For example the pressure-induced structural changes of solids are influenced by the core properties discussed above. These are evident in pseudopotential calculations of the transition pressures for solid–solid phase transformations.

L. J. Sham (*University of California, San Diego, U.S.A.*). For calculation of the superconducting transition temperature in hydrogen, what does Professor Cohen use for electron repulsion? Hydrogen appears to be exotic compared with the materials McMillan considered for μ^*.

M. L. Cohen. Our level of ignorance regarding the electron–electron repulsion parameter for hydrogen is the same as for other metals. We use the standard procedure of scaling μ with r_s and then convert to a μ^* model. In the end the value for atomic metallic hydrogen is not unusual. In this regard, hydrogen is not terribly exotic.

P. B. Allen (*SUNY, Stony Brook, U.S.A.*). BCC–Li would probably be superconducting, but at low T lithium becomes 9R which seems to kill superconductivity. Would this also happen in hydrogen? Does Professor Cohen understand why this happens in Li?

M. L. Cohen. We didn't calculate the electron–phonon coupling constants and superconducting transition temperature for BCC hydrogen because this is an unstable structure, however, I wouldn't be surprised if λ and T_c were larger for BCC than for $9R$ hydrogen. We are examining Li now.

N. W. Ashcroft (*Cornell University, U.S.A.*). There are some quite simple systems (aluminium is an example) that possess moderately high bulk moduli, but otherwise would be characterized as 'weak', i.e. the shear strengths are low. It seems that a real test of 'superhardness' would require both stability analysis of a proposed structure (against, for instance, shear distortion) and if stable a determination of the shear modulus on shear strength. Given this, can Professor Cohen report on the shear strength of the carbon–nitride system, and of the other systems that are being referred to as superhard?

M. L. Cohen. The microscopic property which is the best indicator of hardness is the bulk modulus. However, macroscopic properties such as defects and dislocations effect the hardness of real materials, and as Professor Ashcroft points out the shear strength of a material can be important in this regard. For the covalent materials I discussed this is less of a problem, and for BN and $B\text{–}C_3N_4$ our calculations suggest fairly isotropic properties.

V. Heine (*Cambridge, U.K.*). (*a*) As regards sensitive quantities like band offsets, there have been a few unsatisfactory calculated results when some atoms like Zn and Cd were involved. Work this year by Qteish and Needs in Cambridge has put into the calculations the so-called nonlinear core corrections to the LDA treatment of exchange and correlation. When this is done, much better agreement with experiment is obtained, thus adding to the success story that Professor Cohen has outlined. Of course they are now going on to more complicated situations that are not clear from experiment.

(*b*) In answer to the question that was asked about a pseudopotential for hydrogen: Richard Needs in published calculations with Richard Martin found that the use of a pure Coulomb potential for hydrogen gave better convergent results for energy differences between structures than the use of a hydrogen pseudopotential.

(*c*) Jürgen Hafner and I obtained some interesting indications about the structure of metallic hydrogen using perturbation theory which we never had time to follow up. Now I know perturbation theory is rather ignored in these days of total energy calculations. Moreover the pairwise interactions from perturbation theory expressed in real space has been under a cloud because calculations by different workers in the 1960s and early 1970s gave significantly different results. The latter point has been largely resolved, particularly by Hafner (Hafner & Heine 1986). It is necessary to use a good formula for the exchange and correlation contribution to the dielectric function which satisfies the compressibility sum role. This controls sensitively the radius of the hard core repulsive interaction and hence the shape of the pair potential in the crucial region where the screened core repulsion goes over into the Friedel oscillations with their phase shift involving the pseudopotential. When that is done correctly, one gets pair potentials which yield a great deal of insight into the structures of the elements, even the covalently bonded structures (Hafner & Heine 1983). Anyway, when one calculates such a pair potential for hydrogen in the metallic range of $r_s = 1.2$–1.7 one finds bumps relative to the close packed distance similar to those in Ga, In, Hg which give strange structures there. This is fully in accordance with Professor Cohen's experience that simple structures are unstable. But I found it difficult to come to any clear conclusion about what the coordination number should be and I wonder whether Professor Cohen's search for the correct ground-state structure is at an end.

M. L. COHEN. I agree with Professor Heine's comments. For (*a*), we have had success in calculating the quasi-particle band offset at the (001) interface for GaAs–AlAs heterojunctions (Zhang *et al.* 1990). For many problems it is necessary to use the procedures exchange and correlation interactions. Professor Heine's examples involving Zn and Cd are good ones. Even structural properties are affected by these nonlinear core effects. (*b*) I agree that for most applications it is best to use the full Coulomb potential. (*c*) Kogan and others, in the U.S.S.R. also claim success when using perturbation theory. I am glad to hear that Professor Heine's results for the stability of the simple structures are similar to ours. I do not know whether we have found *the* ground-state structure. At this point the $9R$ structure appears to be stable, and it has a low energy. Perhaps a lower-energy structure will turn up in the future.

Additional references

Hafner, J. & Heine, V. 1983 *J. Phys.* F **13**, 2479–2501.

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Zhang, S. B., Cohen, M. L., Louie, S. G., Tomanék, D. & Hybertsen, M. S. 1990 Quasiparticle band offset at the (001) interface and band gaps in ultrathin superlattice of GaAs–AlAs heterojunctions. *Phys. Rev.* B **41**, 10058–10067.