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Proton pairing, electron pairing, and the phase structure of dense hydrogen

K Johnson and N W Ashcroft

Cornell Center for Materials Research and Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853-2501, USA

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Abstract. Dense hydrogen can be viewed as the superimposition of two standard many-body problems, namely those of the interacting electron gas and the corresponding interacting proton gas, taken at equal average densities. The known low-density instability towards proton pairing appears to be preserved to about $r_s = 1.32$ as inferred from a determination of electronic total energies. Prior to this in density, a transition to a metallic state occurs in which proton pairing persists. In this band-overlap state, electron pairing via a phonon and electronic mechanism is predicted to occur with a transition temperature higher than that found for the eventual monatomic state. This phase is itself preceded by one where electronic symmetry is broken at low temperatures resulting in a state of spontaneous polarization.

1. Introduction

A formal statement of the problem represented by dense hydrogen can be introduced by starting with the canonical fermion problem (figure 1, top panel) of N ($\sim 10^{23}$) electrons, charge $-e$, mass m_e , coordinates $\{\mathbf{r}_{ei}\}$, and spins $\{\hat{s}_{ei}\}$ in a compensating background (charge density $e\bar{\rho} = e(N/V)$ which for volume V is described by the familiar non-relativistic Hamiltonian:

$$\hat{H}_e = \sum_{i=1}^N (-\hbar^2/2m_e)\nabla_{ei}^2 + \frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' \phi_c(|\mathbf{r} - \bar{\mathbf{r}}'|) \{ \hat{\rho}_{ee}^{(2)}(\mathbf{r}, \mathbf{r}') - 2\bar{\rho} \hat{\rho}_e^{(1)}(\mathbf{r}) + \bar{\rho}^2 \}. \quad (1)$$

Here the first term is the total kinetic energy, \hat{T}_e , and

$$\hat{\rho}_e^{(1)}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_{ei}) \quad (2)$$

is the one-electron density operator; also appearing in (1) is the two-particle density operator

$$\hat{\rho}_{ee}^{(2)}(\mathbf{r}) = \hat{\rho}_e^{(1)}(\mathbf{r})\hat{\rho}_e^{(1)}(\bar{\mathbf{r}}') - \delta(\mathbf{r} - \mathbf{r}')\hat{\rho}_e^{(1)}(\mathbf{r}). \quad (3)$$

In specifying the average background density it is convenient to introduce the Wigner–Seitz radius (or RPA parameter) r_s :

$$\frac{4\pi}{3} r_s^3 a_0^3 = (1/\bar{\rho})$$

where the atomic length $a_0 = \hbar^2/m_e e^2$ is also introduced by the fundamental constants appearing in (1). This standard measure r_s will also be used to specify the density of dense

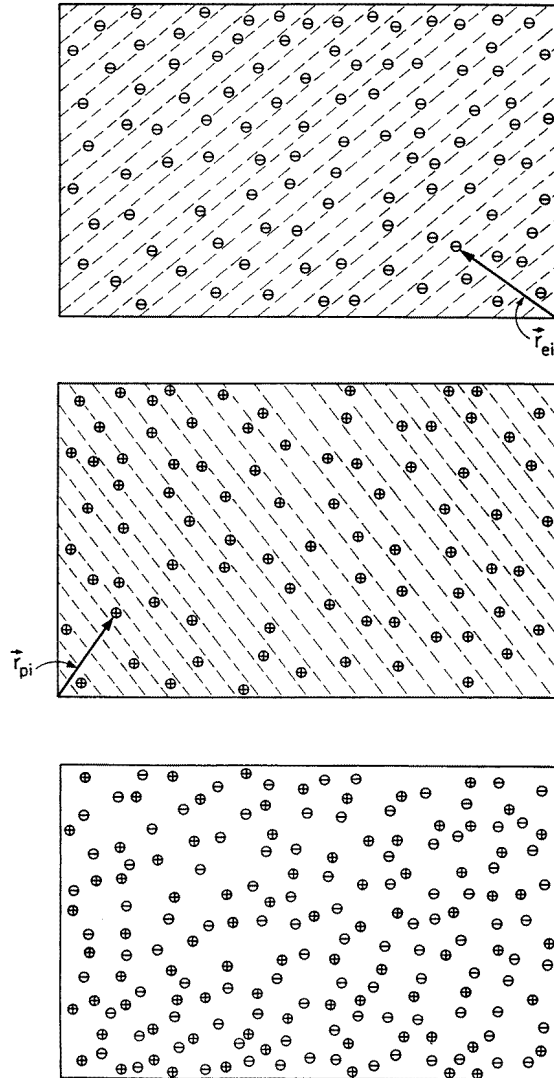


Figure 1. Top panel: an assembly of N interacting electrons, coordinates r_{ei} , in a macroscopic volume V , with a compensating background of charge density $e(N/V) = e\bar{\rho}$. Middle panel: a similar assembly of N interacting protons, coordinates r_{pi} , in the same volume V , now with a compensating background of charge density $-e(N/V) = -e\bar{\rho}$. Bottom panel: electron-gas and proton-gas problems (from the top and middle panels) superimposed in identical volumes V . This construct establishes the hydrogen problem as the interacting electron-gas and proton-gas problems, and mutual interactions between the two.

hydrogen in the description to follow. For values of the density typified by the choice $r_s \sim 1$, it is equally familiar that the non-pairing ground states of (1) are characterized by a homogeneous paramagnetic Fermi liquid, i.e. states of continuous symmetry for which

$$\rho_e^{(1)}(\mathbf{r}) = \langle \hat{\rho}_e^{(1)}(\mathbf{r}) \rangle = \text{constant} = \bar{\rho}$$

and

$$\langle \hat{\rho}_e^{(2)}(\mathbf{r}, \mathbf{r}') \rangle = \langle \hat{\rho}_e^{(1)}(\mathbf{r}) \rangle \langle \hat{\rho}_e^{(1)}(\mathbf{r}') \rangle g^{(2)}(\mathbf{r}, \mathbf{r}') = (\bar{\rho})^2 g_{ee}^{(2)}(|\mathbf{r} - \mathbf{r}'|)$$

where $g^{(2)}$ is now the radial distribution function. Correspondingly

$$E = \langle \hat{T}_e \rangle_0 + \frac{N}{2} \int_V d\mathbf{r} \bar{\rho} \phi_c(r) (g_{ee}^{(2)}(r) - 1)$$

is the ground-state energy and it can usually be written in the form

$$(E/N) = \left\{ \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + E_c(r_s) \right\} \left(\frac{e^2}{2a_0} \right)$$

where the terms represent kinetic, exchange and correlation energies, per electron.

We may observe that if the densities $\bar{\rho}$ are reduced from those equivalent to $r_s \sim 1$ by a factor of 10^6 (or equivalently if the mass of the electron is increased to $10^2 m_e$) then the states of (1) are those of a broken symmetry, a crystal (an example being a Wigner crystal). Then

$$\langle \hat{\rho}_e^{(1)}(\mathbf{r}) \rangle = \langle \hat{\rho}_e^{(1)}(\mathbf{r} + \bar{\mathbf{R}}) \rangle$$

where the $\{\mathbf{R}\}$ are sites of a lattice for which

$$\langle \hat{\rho}_{ee}^{(2)}(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}) \rangle = \langle \hat{\rho}_{ee}^{(2)}(\mathbf{r}, \mathbf{r}') \rangle = \langle \hat{\rho}_e^{(1)}(\mathbf{r}) \rangle \langle \hat{\rho}_e^{(1)}(\mathbf{r}') \rangle g_{ee}^{(2)}(\mathbf{r}, \mathbf{r}').$$

The spin character of this state may be antiferromagnetic, depending on the choice of lattice.

Next, consider a second fermion problem, almost identical in physical character to the electron problem just introduced. In the same volume V (figure 1, middle panel), place N protons, charge $+e$, mass m_p ($=1836m_e$), coordinates $\{\mathbf{r}_{pi}\}$, and spins $\{\hat{s}_{pi}\}$. Again supply a compensating background but now with charge density $-e\bar{\rho} = -e(N/V)$. Then the Hamiltonian for this system is

$$\hat{H}_p = \sum_{i=1}^N (-\hbar^2/2m_p) \nabla_{pi}^2 + \frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' \phi_c(|\mathbf{r} - \mathbf{r}'|) \{ \hat{\rho}_{pp}^{(2)}(\mathbf{r}, \mathbf{r}') - 2\bar{\rho} \hat{\rho}_p^{(1)}(\mathbf{r}) + \bar{\rho}^2 \} \quad (4)$$

where $\hat{\rho}_p^{(1)}$ and $\hat{\rho}_{pp}^{(2)}$ are the proton equivalents of (2) and (3). It is obvious that the elementary length implied by (4) is now $(m_e/m_p)a_0$. For this reason it is clear that if $\bar{\rho}$ is fixed by the electron problem at values leading to an electronic Fermi liquid, then the ground states of (4) are very far into the Wigner-crystal regime.

With these preliminaries, the fundamental problem underlying the physics of dense hydrogen can now be set down. Before doing so, two further remarks are in order on the issue of pairing states. The first is that, though free of intermediaries (for example, phonons), the question of possible ground states of continuous symmetry of (1) but exhibiting off-diagonal long-range-order, and a pairing character, has arisen [1]. The second is that in a completely analogous way it can be asked whether the crystalline phases of (1) (and even of (4)) are necessarily those of a Bravais lattice, or whether, for example crystalline structures with paired bases might also be preferred [2]. Given these hints of intrinsic pairing structures we now imagine superimposing the problems represented by (1) and (4) (figure 1, bottom panel); then the ensuing problem is described by the Hamiltonian

$$\hat{H} = \hat{H}_e + \hat{H}_p - \int_V d\mathbf{r} \int_V d\mathbf{r}' \phi_c(|\mathbf{r} - \mathbf{r}'|) (\hat{\rho}_e^{(1)}(\mathbf{r}) - \bar{\rho}) (\hat{\rho}_p^{(1)}(\mathbf{r}') - \bar{\rho}) \quad (5)$$

and since the respective backgrounds in (1) and (4) exactly cancel it is also clear that this is entirely equivalent to

$$\hat{H} = \sum_{\alpha} \left\{ \hat{T}_{\alpha} + \frac{1}{2} \sum_{\alpha'} (-1)^{\alpha+\alpha'} \int_V d\mathbf{r} \int_V d\mathbf{r}' \phi_c(|\mathbf{r} - \mathbf{r}'|) \hat{\rho}_{\alpha\alpha'}^{(2)}(\mathbf{r}, \mathbf{r}') \right\} \quad (6)$$

where $\alpha = 1, 2$ denote electrons (e) and protons (p) respectively, and

$$\hat{\rho}_{12}^{(2)}(\mathbf{r}, \mathbf{r}') = \hat{\rho}_{ep}^{(2)}(\mathbf{r}, \mathbf{r}') = \hat{\rho}_e^{(1)}(\mathbf{r})\hat{\rho}_p^{(1)}(\mathbf{r}').$$

Note that as with (1) and (4), the fundamental Hamiltonian for hydrogen, (4) or (5), has considerable symmetry.

The problems defined either by (5) or (6) constitute the dual fermion assembly represented by condensed phases of hydrogen. With the replacement $m_p \rightarrow m_d$ (the mass of the deuteron) in (4) and a fundamental change in quantum statistics, the Hamiltonian

$$\hat{H} = \hat{H}_e + \hat{H}_d - \int_V d\mathbf{r} \int_V d\mathbf{r}' \phi_c(|\mathbf{r} - \mathbf{r}'|)(\hat{\rho}_e^{(1)}(\mathbf{r}) - \bar{\rho})(\hat{\rho}_d^{(1)}(\mathbf{r}') - \bar{\rho}) \quad (7)$$

defines the corresponding fermion–boson assembly represented by the condensed phases of deuterium. Dual fermion problems arise in a completely different context, for example in nuclear physics, where the four-particle problem represented by the alpha particle (two protons and two neutrons) has a notable stability, which finds a parallel in the two-electron–two-proton system emerging at low densities as the hydrogen molecule. The primary task is now evident: it is to start with (5), (6) or (7), and to account for, and if possible predict, the equilibrium phase structure of hydrogen as a function of r_s and T . It is also to account for the response properties (e.g. static and dynamic conductivities) of these phases.

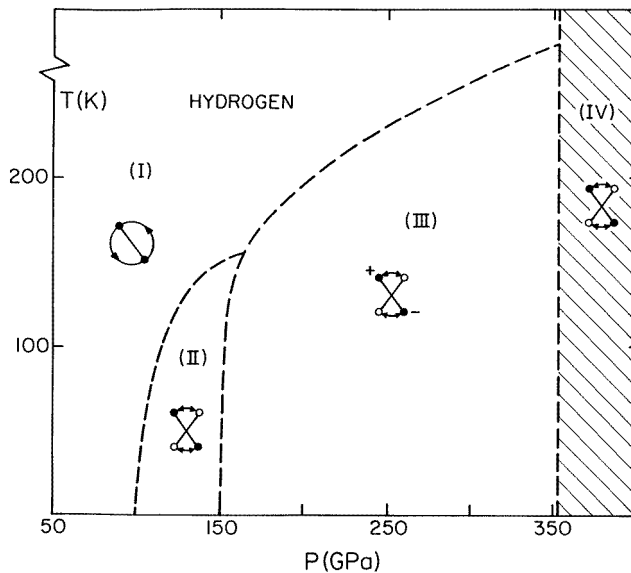


Figure 2. An approximate phase diagram of dense hydrogen. Phase I (the low-pressure phase) is crystalline with proton and electron pairs persisting in rotational states. In phase II there is incomplete rotation, or wide-angle libration. Phase III is characterized by spontaneous polarization or charge-density-wave behaviour, but again is accompanied by wide-angle libration. In phase IV (again, the proton dynamics is important) a band-overlap transition appears to take place. The phase is semi-metallic and probably also superconducting. Note the break in the temperature scale. The upper boundaries in both T and P are currently uncertain.

2. Near ground states of dense hydrogen

Dense phases of hydrogen have been probed experimentally under conditions corresponding to $\bar{\rho}/\bar{\rho}_0 \sim 10$ and temperatures currently reaching as high as $T \sim 3000$ K. For these conditions, significant conductivity is reported [3], in some contrast to the situation near the ground state where to date hydrogen remains resolutely insulating to pressures reported to be as high as 340 GPa [4]. Even in the high-temperature phase, probably a translational fluid ($\rho_p^{(1)}(\mathbf{r}) = \langle \hat{\rho}_p^{(1)}(\mathbf{r}) \rangle = \bar{\rho}$), there is evidence that the protons remain substantially paired; i.e. in

$$\rho_{pp}^{(2)}(\mathbf{r}, \mathbf{r}') = (\bar{\rho})^2 g_{pp}^{(2)}(|\mathbf{r} - \mathbf{r}'|)$$

the pair distribution $g_{pp}^{(2)}(|\mathbf{r} - \mathbf{r}'|)$ is expected to be characteristic of a diatomic fluid. (It is the distribution functions, $g_{pp}^{(2)}$, and their extensions at higher order that have physical significance, and not the low-density constructs H , H^+ , H_2 , H_2^+ , etc, which have no precise definition at densities characterized by $r_s \sim 1$.) At lower temperatures, where the physical properties of dense hydrogen have mainly been elucidated by diamond anvil experiments, figure 2 summarizes the phase diagram with phase I (also called the low-pressure phase) corresponding to a state with proton pairs occupying crystalline sites, but also persisting in states where angular momentum is a quite good quantum number. In crossing into phase II (also referred to as the broken-symmetry phase) the latter is no longer the case, and in classical terms the proton pairs execute wide-angle libration about the time-average crystalline sites. To reach this phase, considerable compression is required (as can be seen from figure 2), yet as noted the state is still insulating. It also remains so as the boundary into phase III (or the H-A phase) is crossed. The chief characteristic of this phase is that on entering it there is (a) a notable and mass-dependent *drop* in the principal vibron frequency, and (b) an even more striking onset of infrared activity. Both phenomena can be driven away by sufficient increase in temperature; the onset density of both also appears to be largely mass independent. These observations already begin to argue for a substantially electronic explanation for the new ordering represented by phase III even though it is manifestly obvious that the proton (or deuteron) dynamics is playing an important role. For all three phases, proton pairing appears secure, as it does for a possible phase IV (to be discussed below); it is suggested that this is characterized by a band-overlap transition into a semi-metallic state. Again, electronic ordering is anticipated at low temperatures: specifically electron pairing and the onset of superconductivity [5].

In treating (5) or (6) (or indeed (7)) from the standpoint of a partition function

$$Z = \text{Tr} e^{-\beta \hat{H}}$$

the approaches divide simply into those which invoke a standard adiabatic separation of electronic and protonic timescales, and those which do not. Because of the simplicity and symmetry of \hat{H} for the hydrogen problem, considerable progress can be made with the latter when the partition function is established as a coherent-state functional integral. The third term in (5) is then crucial in establishing pairing fields for both protons and electrons in states of both continuous symmetry and crystalline symmetry [6]. Electrons and protons can also be treated on a completely equal footing by quantum Monte Carlo methods (Natoli *et al* [7]).

Within the Born–Oppenheimer approximation the low-temperature phases of hydrogen present an average crystalline arrangement on proton timescales, but on electronic timescales they also present a problem considerably more complex than that normally encountered in addressing the electronic structure of a solid disturbed by ordinary phonons. For example

in phase I the motion of proton pairs is fully rotational, while in phase II it is librational, with large-angle excursions as noted. Incorporating these effects into a self-consistent single-particle description (such as a band-structure) remains a largely unsolved problem. Nevertheless the single-particle picture for the electronic structure of dense hydrogen has mainly dominated the interpretation of much of the data accumulated on dense hydrogen. And within the single-particle view it is the band-structure model, involving the assumption of infinitely massive protons, that has likewise dominated.

For fixed proton positions, the many-electron problem can be reduced to an equivalent single-particle description embodied in the formally exact Kohn–Sham equation which for a periodic system takes the form

$$(\hat{T} + \hat{V} + \hat{V}_{xc})\psi_{nk}(\mathbf{r}) = \varepsilon_{nk}\psi_{nk}(\mathbf{r}) \quad (8)$$

with the single-particle states ψ_{nk} possessing the Bloch character for band n and crystal momentum \mathbf{k} . In (8), \hat{V} includes the interactions with protons and the Hartree contributions from other electrons. As in its application to other systems, the Kohn–Sham equation requires a stipulation of the exchange–correlation potential, \hat{V}_{xc} , a functional of the one-electron (electronic) density $\rho_e^{(1)}(\mathbf{r})$. At densities $\bar{\rho}$ typified by $r_s \simeq 1.6$, the electronic energy bands resulting from solutions of the Kohn–Sham equation display a notable similarity to moderately distorted free-electron bands, in spite of the fact that the electronic density $\rho_e^{(1)}(\mathbf{r})$ is extremely inhomogeneous. Given this, it is straightforward to argue [8] from the necessity to prevent band overlap in the retention of an overall insulating state that for the common structures (hexagonal and related) the molecular axes should be neither parallel to the c -axis, nor to the a - and b -axes. Lowering of energy can also be predicted to occur [9] for orthorhombic rather than hexagonal structures. Thus tilted arrangements in orthorhombic cells would seem to be preferred, as confirmed originally by Kaxiras and Broughton [10] and by many ensuing studies [11], but mainly within the local density approximation to exchange–correlation contributions.

These show that to quite high densities hydrogen strongly retains its proton pairing, and that among the crystal classes the orthorhombic structure is indeed also strongly indicated (this apparently holding true when the proton dynamics is reintroduced). Within the orthorhombic structures it is the $cmca$, $cmc2_1$, and $c2/m$ forms that also seem most favoured [12] at least within limited relaxation of the corresponding orthorhombic cells. These have bases of two sets of proton pairs, and a remarkable feature of the arrangement is that, at ninefold compression and above, the twin sets of basis pairs can be identified with sublattices which can develop opposing spontaneous polarization. That this might be expected can be attributed to the fact that in terms of the average linear dipole polarizability of the highly stable (two-electron, two-proton) problem that we normally identify as the hydrogen molecule, the relative volumetric compression achievable in experiment is unusually high [13]. In this polarized state the overall gap is increased slightly over its value for an equivalent unpolarized state, but nevertheless the effect of further increase in density is to continually decrease the *overall* gap.

This viewpoint leads to the expectation of an eventual transition to a band-overlap state (for fixed protons) where, in the single-particle picture, a Fermi surface is established in the ground state. Of crucial importance is the density (or pressure) at which the gap is projected to close. The issue is therefore the degree to which current electronic structure methods are capable of predicting band-gaps, either direct or indirect, for a given structure. As is well known, the local density approximation (LDA) to the exchange and correlation contributions to the ground-state energy is on the whole reasonably good, though certainly improvable (and several gradient correction methods attempt this). However, it performs

considerably less well for excited states, predictions of band-gaps being a case in point, and clearly a key one for the present study. For hydrogen the corrections are known to be considerable, from the work of Chacham *et al* [14]. The quasi-particle energies in (8) are in principle determined by the solution of Dyson's equation:

$$(\hat{T} + \hat{V})\psi_{nk}(\mathbf{r}) + \int_V d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; \varepsilon_{nk})\psi_{nk}(\mathbf{r}') = \varepsilon_{nk}\psi_{nk}(\mathbf{r}) \quad (9)$$

with Σ the self-energy operator for electrons. An approximation going beyond the LDA is to follow Hedin's [15] suggestion and to simply evaluate Σ as the leading term in the Coulomb interaction, itself dynamically screened. This is referred to as the *GW*-approximation, and though it is itself an incomplete representation of many-body effects, it leads to very considerable improvements over the local density approximation. A difficulty in the practical implementation of this approximation for periodic systems is the necessity of inverting the dielectric matrix which enters the screened interaction. To circumvent this (for hydrogen and for other systems), a further development of the extreme tight-binding method of Sterne and Inkson [16] has been recently introduced [17] which obviates much of the computational complexity, yet remains accurate (in terms of band-gap corrections) at the level of about 0.1 eV. The method requires information on the dielectric behaviour of the system, and in the case of hydrogen this can be taken from experiment [18] and also from the paper by Chacham *et al* [14]. For a given choice of structure it is then possible to systematically correct the LDA gaps for dense hydrogen. Not surprisingly, they are increased, and quite significantly [13]. Nevertheless, they continue to decline with increase in density, and for the *cmc2*₁ structure vanish at $r_s \sim 1.38$, to be compared with $r_s = 1.46$ for the LDA. Note, again, that this corresponds to fixed or infinitely massive protons.

With respect to structural selection, pairing forms are consistently found to be energetically favoured over monatomic phases, persisting to quite high densities including densities progressing into an eventual band-overlap (semi-metallic) state. Pairs are arranged in space in a centred orthorhombic cell [7] (the *cmc2*₁ structure for phase III), and for the calculations that we have carried out to date this appears to be significantly more stable than other competitor structures [17]. This appears to hold true for calculations which invoke a complete Coulombic electron-proton interaction, and also pseudopotential representations of it. A detailed description of these calculations is given in reference [17], but it may be noted that energy cut-offs for plane-wave basis sets, and \mathbf{k} -space grids have been chosen such that total energies are converged at a level of better than 1 meV per proton. As noted, for incompletely relaxed orthorhombic cells the *cmc2*₁ structure is preferred in phase III, but only by a small amount over *c2/m*. Figure 3 shows an example of the energy bands for this structure for both $r_s = 1.51$ where hydrogen is clearly an insulator, and at $r_s = 1.45$ where band overlap has occurred and a metallic state ensues. It is the gaps in the insulating phase that are corrected by the modified [17] Sterne-Inkson method.

In an earlier study [12] it was found that a state of spontaneous polarization develops in the *cmc2*₁ structure (now to be associated with the infrared-active phase III), and proton pairs actually moved off site when the phase II-phase III boundary was crossed at low temperatures. Large librational motion in this state effectively renders the associated electronic problem as one corresponding to instantaneous disorder [19]. No long-range coherence in electron phase can therefore be expected, but instead there can be a consequent localization by disorder (reinforced by correlation) if the bandwidth is within suitable bounds. Because of this, a mean-field treatment of interactions, developed through multipoles connecting phase-decoupled ($2e + 2p$) units is a reasonable first step [20]. The trend in dipolar polarization, in which the long-range energy associated with self-sustaining

polarization is significant, is also confirmed in the new sequence of calculations, and indeed is found to continue until the gap closes, and hydrogen passes into a band-overlap state. It is suggested that this state be identified as a possible phase IV, a semi-metallic phase where the spontaneous polarization is found to be lost and the preferred structure is now *cmca*. The loss of polarization might be anticipated physically because the presence of free charge leads immediately to the possibility of screening of the long-range fields which sustain the insulating polarized state in a self-consistent manner.

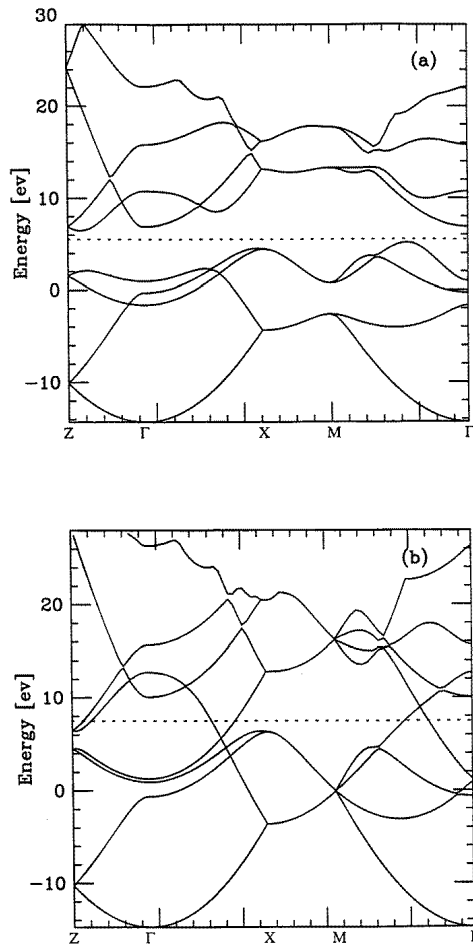


Figure 3. Energy bands for dense hydrogen as determined by density functional theory within the local density approximation and for the *cmc2₁* structure. In (a) the average density corresponds to $r_s = 1.51$, and in (b) it corresponds to $r_s = 1.45$. The dashed lines indicate in each case the zero-temperature chemical potential (the Fermi energy in the metallic phase).

As noted, proton pairing survives the transition to the metallic phase. To gain some insight into the observed persistence of proton pairing at high densities, consider the problem represented by Hamiltonian (6) but focus attention on just two protons (designate their coordinates by r_{p1} and r_{p2} and take their separation to be $\mathbf{R} = r_{p1} - r_{p2}$). Now let the charges of all other protons ($r_{pi} \neq r_{p1}, r_{p2}$) be replaced by a rigid continuum. Since we

are in a thermodynamic limit, this problem can be represented by the Hamiltonian

$$\hat{H}(\mathbf{R}) = \hat{H}_e - \int_V d\mathbf{r} \langle \hat{\rho}_e^{(1)}(\mathbf{r}) - \bar{\rho} \rangle \phi_e(\mathbf{r}) - \int_V d\mathbf{r} \langle \hat{\rho}_e^{(1)}(\mathbf{r}) - \bar{\rho} \rangle \phi_e(\mathbf{r} - \mathbf{R}) \quad (10)$$

where one of the protons can be taken at the origin, and both can be taken as infinitely massive, as above. The proton separation now becomes a parameter in a largely electronic Hamiltonian, and the Hellmann–Feynman theorem applies. Stabilization can therefore occur for fixed $\bar{\rho}$ as a function of separation at a point where [18]

$$e^2/R^2 = \int_V d\mathbf{r} \langle \hat{\rho}_e^{(1)}(\mathbf{r}) - \bar{\rho} \rangle_R \left(-\frac{\partial}{\partial R} \phi_e(\mathbf{r} - \mathbf{R}) \right). \quad (11)$$

In (11), an approximate guide to $\langle \hat{\rho}_e^{(1)}(\mathbf{r}) \rangle$ and the solution for R can be inferred from the electron density resulting from a Heitler–London approach when the protons are separated by \mathbf{R} , but the total electron density also includes a constant background density associated with \hat{H}_e . As with the free molecule, the exchange enhancement of $\langle \hat{\rho}_e^{(1)}(\mathbf{r}) \rangle$ in the region between the protons (the enhancement over the Hartree form) leads to considerable bonding. Unique to hydrogen is the fact that the interaction entering this stability condition is the full Coulomb potential (in other systems it will at best be a pseudopotential).

This argument can be extended somewhat by returning to the full Hamiltonian (6) and again extracting a single proton pair (with separation \mathbf{R}) and then proceeding to the change in the electronic problem that ensues when this pair suffers a change in separation \mathbf{R} , all other protons being held fixed. Once again the Hellmann–Feynman theorem applies and a stabilization is anticipated, though the condition is more complex than (11) because of the additional interactions arising from the other and largely more distant protons. But note that $\langle \hat{\rho}_e^{(1)}(\mathbf{r}) \rangle$ also now contains contributions associated with the very same protons, and if these are aggregated with the corresponding protons the net contribution corresponds to neutral objects. For this reason, the stabilizing condition is then expected to be not very different from (11). The existence of a pairing state that is bound overall is clearly conditional on the neglect of proton dynamics. Within the Born–Oppenheimer separation, the Hellmann–Feynman theorem can again be applied to the problem within the stipulation that $\langle \hat{\rho}_e^{(1)}(\mathbf{r}) \rangle$ represents the electronic density in a fully dynamic context. But aside from the issue of proton dynamics, the arguments indicating a propinquity towards pairing evidently requires no especial distinction to be made between metallic and insulating phases.

3. Electronic instability and pairing

The free hydrogen molecule ($2e + 2p$) has very significant binding energy against separation into a pair of hydrogen atoms $2(e + p)$. Evidently a pair of protons can be very effectively bound by a pair of electrons, a pairing that persists with notable tenacity to very high density ($\bar{\rho}/\bar{\rho}_0 \sim 10$). Given the evident symmetry of (6) (and its states) under the interchange $m_e \leftrightarrow m_p$, it is clear that the question might be inverted; that is, we may ask instead whether conditions can be found (on density and temperature) where pairing or indeed other ordering can be induced in the electrons by virtue of the proton dynamics. In addressing this issue, note that from a crystalline one-electron perspective the pairing of protons implies that regardless of structure an integral number of bands can be exactly filled in the ground state; departure from this necessary condition for insulating behaviour occurs only if the density $\bar{\rho}$ is compatible with band overlap. A recent parallel here is the even-valence element sulphur which, at high pressures, undergoes an insulator-to-metal transition, with the metallic phase immediately exhibiting superconductivity (with a

transition temperature of some 10.1 K, but rising with further increase in pressure [21]). The Raman effect [22] shows that characteristic phonon frequencies are not exceptional, being in the range 400–500 cm⁻¹. The metallic phase of sulphur is of the band-overlap type, as is being argued for hydrogen. However, for hydrogen the corresponding frequencies are ~4000 cm⁻¹ for optic modes and 1600 cm⁻¹ for acoustic modes (and characteristic densities of states for the electronic structure can be considerably higher).

Of particular interest in both systems is the role of effective electron–electron interactions in the common multiband (and specifically electron–hole) context. For it has been shown [23] that even in the absence of exchange bosons, correlated charge fluctuations between electrons and holes can lead to weakening of the net electron–electron interaction over what is expected from the screening arising from each band separately. The principal physical effects of this are twofold: first, in the complete absence of intermediaries (phonons or other exchange bosons) pairing ground states can be preferred, the ensuing transition temperature then depending on the electron and hole masses and densities, as is expected. Second, subsequent inclusion of proton dynamics through harmonic phonons (with frequency scales as above, and with large electron–phonon coupling) then leads in the paired metallic phase of hydrogen to very significant transition temperatures. Accordingly in phase IV of figure 2, where it appears as noted that energetically the *cmca* class of structure is preferred, then because of the primarily electron–hole character of the ensuing band-overlap state, pairing of electrons is also expected. The reason for this can be found from examination of the Eliashberg equation for the pairing function $\Phi_\ell(k, i\omega_n)$ of ℓ -wave superconducting order, namely

$$\Phi_\ell(k, i\omega_n) = -k_B T \sum_{n'} \int_0^\infty dk' K_\ell(k, i\omega_n; k', i\omega_n') \Phi_\ell(k', i\omega_n'). \quad (12)$$

In (12) the kernel is

$$K_\ell(k, i\omega_n; k', i\omega_n') = \frac{k'}{4\pi^2 k} |G(k', i\omega_n')|^2 \int_{|k-k'|}^{k+k'} dq P_\ell\left(\frac{k^2 + k'^2 - q^2}{2kk'}\right) q V_{\text{eff}}(q, i\omega_n - i\omega_n') \quad (13)$$

where $V_{\text{eff}}(q, i\omega)$ is the irreducible electron–electron interaction. If v_q is the bare Coulomb interaction, then in the band-overlap context appropriate to phase IV, the effective electron–electron interaction in the *absence* of phonons is

$$V_{\text{eff}} = v_q + \frac{v_q^2(1 - G_{11}^s)\Pi_0^{(1)}}{1 - v_q(G_{11}^s)\Pi_0^{(1)}} - \alpha \frac{v_q^2(G_{11}^a)^2\Pi_0^{(1)}}{1 + v_q G_{11}^a \Pi_0^{(1)}} + v_{12}^2 \Pi^{(2)} \quad (14)$$

where $\Pi_0^{(1)}$ is the Lindhard approximation to the density–density response function for band 1 but modified to include self-energy effects. In (14), $\alpha = 3$ or -1 for singlet or triplet pairing, $v_{12} = (1 - G_{12}^s)v_q/(1 - v_q(1 - G_{11}^s)\Pi_0^{(1)})$, and $\Pi^{(2)}$ is the density–density response function for band 2. The form of effective interaction embodied in (14) is an extension to the electron–hole context of the Kukkonen–Overhauser approximation [24]. The quantities $G^\sigma(q, i\omega)$ are local field factors; the function $G(k, i\omega_n)$ appearing in (13) is the Green’s function for fully interacting electrons and is related to the self-energy (see equation (9)) by

$$\Sigma(k, i\omega_n) = -k_B T \sum_{n'} \int \frac{dq}{(2\pi)^3} G(q, i\omega_n) V_{sc}(q - k, i\nu_n - i\omega_n).$$

The introduction of phonons into this otherwise wholly electron picture is now straightforward. It amounts to adding

$$V_{\text{ph}} = \frac{-\alpha}{(1 + (q/2k_F)^2)} \frac{\omega_q^2}{\omega^2 + \omega_q^2}$$

where the phonon frequencies are given by $\omega_q^2 = \beta q^2 / (1 + \gamma q^2)$. The quantity α can be fixed by requiring a correct determination of the electron–phonon coupling parameter, β is determined by the Debye temperature, and γ is fixed by $\langle \omega \rangle$.

As hydrogen is induced by pressure to enter phase IV (the proposed paired-proton metallic phase), correlated charge fluctuations arising from the last term in (14) (which is *attractive*) are predicted to give rise to electron pairing, even in the absence of phonons [21]. If phonons are included and a value of 1.5 taken for the electron–phonon coupling parameter (as suggested by Barbee *et al* [25]), then with a valley degeneracy of 2, pairing can occur first in the electron band, and at $r_{\text{se}} = 3$ the transition temperature is as high as 300 K. It can rise even further at lower electron band densities, a point that focuses attention on the one-electron structure, and once again on the details of the average proton arrangement. Superconductivity is therefore being driven both by phonons and by correlated charge fluctuations.

4. Emerging physical issues

It is quite clear that a more precise determination of the phase boundaries requires inclusion of the proton and electron dynamics on an equal footing. This was already evident some time ago [26], but is all the more apparent now since energy differences between competing structures are seen to be much smaller than characteristic phonon energies. As noted above, the issue of electron pairing is also very much dependent on the self-consistent one-electron bands, and again this is a structural issue. But another interesting issue which is emerging concerns the nature of the elementary excitations at the point in density (or pressure) where the self-consistent gap crosses the phonon energy scale. Note that the vibron (or optical phonon) scale is typically 1/2 eV, with the result that this confluence will occur in phase III, i.e. preceding the transition to the semi-metallic state predicted on the basis of the adiabatic approximation. At this point, electron and phonon states will become significantly mixed, and since away from the confluence both are involved in the balance of energies determining the overall structure, we are led to expect further phase structure to occur before phase IV is reached (possibly of polaronic character). Perhaps the most important point to emerge now is the evident necessity to approach the issue of the electronic structure in dense hydrogen from a perspective that goes beyond the local density approximation to density functional theory. In what has been discussed above, it is the gap structure only that has been corrected. From the significant shifts seen, it is clear that a *GW*-procedure for the entire energetic problem is now called for. However, within the LDA it appears that phase IV may be fairly restricted in its domain, for the calculations are already suggesting that a transition to a monatomic phase may occur at pressures typified by 400 GPa (with β -Sn and Cs-IV being competitive candidates).

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