

Order in dense hydrogen at low temperatures

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By increase in density, impelled by pressure, the electronic energy bands in dense hydrogen attain significant widths. Nevertheless, arguments can be advanced suggesting that a physically consistent description of the general consequences of this electronic structure can still be constructed from interacting but state-dependent multipoles. These reflect, in fact self-consistently, a disorder-induced localization of electron states partially manifesting the effects of proton dynamics; they retain very considerable spatial inhomogeneity (as they certainly do in the molecular limit). This description, which is valid provided that an overall energy gap has not closed, leads at a mean-field level to the expected quadrupolar coupling, but also for certain structures to the eventual emergence of dipolar terms and their coupling when a state of broken charge symmetry is developed. A simple Hamiltonian incorporating these basic features then leads to a high-density, low-temperature phase diagram that appears to be in substantial agreement with experiment. In particular, it accounts for the fact that whereas the phase I-II phase boundary has a significant isotope dependence, the phase II-III boundary has very little.

At low temperatures and ordinary pressure, crystalline hydrogen has a mean electronic density that exceeds the valence electron density of all the alkali metals and even the alkaline earths under equivalent conditions. However, it is a ground state insulator retaining this physical characteristic at densities an entire order of magnitude higher than its one atmosphere value. Under these compressions application of band theory for rigorously *static* lattices shows clearly that the electronic energy bands of hydrogen are appreciably wide, indicating significant overlap between the standard orbitals invoked to describe the low density phases. Yet much of the electronic charge remains well localized in the vicinity of a Bohr radius from the protons, and there is evidence that the currently accessible part of the low temperature, high density phase diagram can still be understood in terms of interactions originating with multipole expansions associated with effectively localized states and a continuing preservation of the strongly inhomogeneous character of the microscopic electron density $\rho_e^{(1)}(\mathbf{r})$. The deeper understanding of this notion, and its consequences, constitutes the bulk of what follows, but starting from an elementary observation that a macroscopic neutral quantity of hydrogen is but a dual Fermion assembly of electrons and protons, and that the dynamics of the latter have considerable influence on the former.

The Dense Hydrogen Problem

The quantum mechanics of $N(\sim 10^{23})$ electrons in a uniform compensating charged continuum of volume V is a well studied problem, though debate still continues on the nature of its low density states (especially in reduced dimensionality). If $v_c(r) = e^2/r$ is the fundamental Coulomb interaction, and if $e\bar{\rho} = e(N/V)$ is the corresponding rigid continuum charge density, then the Hamiltonian for this system, to be taken as canonical and neutral overall, is

$$\hat{H}_e = \hat{T}_e + \hat{V}_e \quad [1]$$

where for $m = m_e$ (the electron mass)

$$\hat{T}_e = \sum_{i=1}^N (-\hbar^2/2m)\nabla_{i\mathbf{e}}^2 \quad [2]$$

and

$$\hat{V}_e = \frac{1}{2} \int_V d\mathbf{r} \int_V d\mathbf{r}' v_c(\mathbf{r} - \mathbf{r}') \{ \hat{\rho}_e^{(2)}(\mathbf{r}, \mathbf{r}') - 2\bar{\rho}\hat{\rho}_e^{(2)}(\mathbf{r}) + \bar{\rho}^2 \}. \quad [3]$$

Here the electron coordinates are $\{\mathbf{r}_{ei}\}$ in terms of which the one-particle density operator (associated with electron-background interactions in Eq. 3) is

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

The electron-electron interactions in Eq. 3 are associated with the two-particle density operator

$$\hat{\rho}_e^{(2)}(\mathbf{r}, \mathbf{r}') = \hat{\rho}_e^{(1)}(\mathbf{r})\hat{\rho}_e^{(1)}(\mathbf{r}') - \delta(\mathbf{r} - \mathbf{r}')\hat{\rho}_e^{(1)}(\mathbf{r}). \quad [4]$$

The ground states of Eq. 1, which has no explicit reference to the spin of the electrons, include most notably the paramagnetic Fermi liquid for which $\langle \hat{T}_e \rangle > \langle \hat{V}_e \rangle$ is required, and for which

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

The fundamental constants in Eqs. 2 and 3 define a familiar length $\hbar^2/m_e e^2$ when m is taken as the electron mass, m_e . It is the standard Bohr radius and it may be used to fix the density of the system in terms of the dimensionless quantity r_s defined by $(4\pi/3)r_s^3 a_0^3 = 1/\bar{\rho} = V/N$. For the Fermi liquid the condition $\langle \hat{T}_e \rangle > \langle \hat{V}_e \rangle$ is generally met when $r_s \leq 0(1)$. In what follows, it is r_s that will be taken as the measure defining the overall density.

Though Eq. 1 has considerable symmetry, there are broken symmetry states at low density, where $\langle \hat{T}_e \rangle < \langle \hat{V}_e \rangle$, the Wigner crystal being a prominent example. For this case

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

where $\{\mathbf{R}\}$ is the set of all vectors of a lattice. In order for the electronic density to be periodic, it is not necessary that the Wigner crystal be a Bravais lattice (1). In three dimensions it appears (2) that to achieve crystalline states the values of r_s need to be greater than ≈ 40 . Low densities also admit of the possibility of magnetically ordered phases.

A problem with completely identical physical characteristics (and with precisely the same Hamiltonian as in Eqs. 1-3) is obtained if electrons (charge $-e$ and mass $m = m_e$) are replaced by protons (also Fermions but now with charge $+e$ and mass $m = m_p = 1,836m_e$) with the sign of the background charge density simply being reversed. For this system the fundamental unit of length is $a_0/1,836$, and it follows that if $\bar{\rho}$ is so chosen that the states of an *electron* system with this density are those of a Fermi liquid then for the same $\bar{\rho}$ the proton system is well into the Wigner crystal regime.

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From these two familiar problems the Hamiltonian \hat{H} describing all phases of hydrogen is readily determined: Fix r_s , or equivalently a background density $e\bar{\rho}$, and establish the electron problem, \hat{H}_e . For a background density $-e\bar{\rho}$, now establish the proton problem, \hat{H}_p . Permit these two neutral systems to occupy a common volume and then determine the mutual interactions \hat{H}_{ep} between them. On canceling the backgrounds we clearly arrive at the initiating canonical problem of N electrons and N protons (with mutual Coulomb interactions), i.e., a macroscopic quantity of hydrogen in a volume V . But in terms of the separate equivalent problems the Hamiltonian is also immediately seen to be

$$\hat{H} = \hat{H}_e + \hat{H}_p - \hat{H}_{ep}, \quad [5]$$

where

$$\hat{H}_{ep} = \int_V d\mathbf{r} \int_V d\mathbf{r}' v_c(\mathbf{r} - \mathbf{r}') (\hat{\rho}_p^{(1)}(\mathbf{r}) - \bar{\rho}) (\hat{\rho}_e^{(1)}(\mathbf{r}') - \bar{\rho}) \quad [6]$$

or equivalently

$$\hat{H} = \hat{H}_e + \hat{H}_p - (1/V) \sum_{\mathbf{k} \neq 0} v_c(\mathbf{k}) \hat{\rho}_e^{(1)}(\mathbf{k}) \hat{\rho}_p^{(1)}(-\mathbf{k}), \quad [7]$$

where in three dimensions $v_c(k) = 4\pi e^2/k^2$ and

$$\hat{\rho}_\alpha^{(1)}(\mathbf{k}) = \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_{\alpha i}).$$

The Hamiltonian represented by Eq. 5 has considerable symmetry, and its form also leads to scaling relations for both the thermodynamic and correlation functions (3). In what follows, physically relevant densities for dense hydrogen will imply values of $r_s \geq 1.35$, corresponding to the highest levels of densification achieved in recent experiments (4,5). Under these conditions the coupling \hat{H}_{ep} remains far from small, and as a consequence perturbation methods are required to proceed beyond linear response (6).

Fig. 1 shows a limited region of the phase diagram representative of dense hydrogen inferred from considerable experimental and theoretical effort (7–17). Many of the structural characteristics of dense hydrogen are summarized in recent reviews (14, 15) that augment the earlier review by Silvera (18). The transition (for $T \sim 0$) at ≈ 150 GPa for both hydrogen and deuterium is notable, for it corresponds to an increase in proton-pair polarization that is about an order of magnitude greater than the phase II value (16). At this transition there is also a discontinuous *downshift* (19) of the vibron frequency (by $\approx 100 \text{ cm}^{-1}$). The I–II and II–III transitions are both reported to be first order; on the other hand, the I–III transition is interpreted as first order up to a certain point on the phase line. Beyond it both the nature and order of the transition remain to be clarified. It may be noted that deuterium orders to phase II from phase I at pressures considerably lower than those found for hydrogen, an effect that can be attributed immediately to the larger mass of deuterium and in consequence a lower rotational zero point energy (see below). However, the fact that both for dense hydrogen and dense deuterium (with double the mass) there is a prominent transition at a near common density suggests strongly that its origin is primarily electronic, and thus not significantly dependent on center of mass motion of proton or deuteron pairs. This is central to establishing an approximate analysis which focusses on electronic structure which may well be influenced by the much lower energy internal (especially rotational) dynamics. In what follows it will be shown that these fundamental phase characteristics emerge from a state-dependent multipole representation of the interactions associated with Eq. 5, these self-consistently linked to charge localized by disorder. The analysis is therefore carried out under the assumption

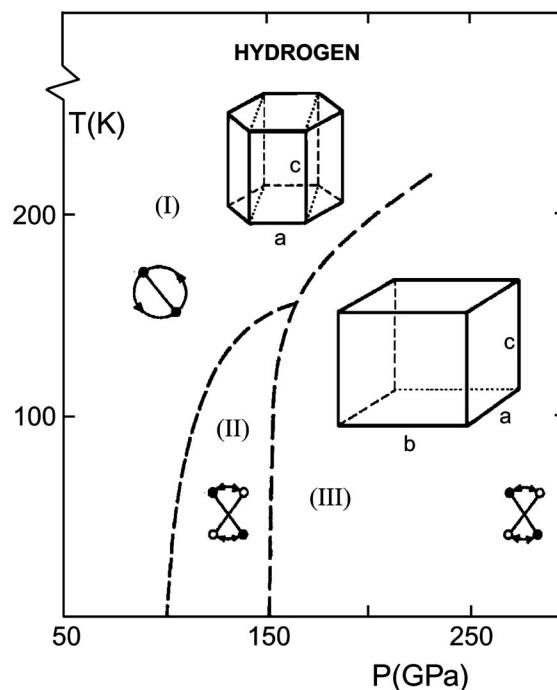


Fig. 1. Summary of the approximate form of the phase structure of dense hydrogen at relatively low temperatures. Phase I (also known as the low-pressure phase) conforms to the hexagonal class of structures and is a phase where angular momentum remains a good quantum number. In phase II (or the broken symmetry phase) the structure is possibly Pa3, and the rotation is hindered but is nevertheless of quite wide angle. In phase III (also called the HA phase) the structure is predicted to be in the orthorhombic class and there is still wide-angle libration, but unlike phase II there is also strong infrared activity linked to an apparent permanent polarization of the $2e + 2p$ units.

tion that translational zero-point energies change only in a relatively minor way in the vicinity of phase boundaries that may otherwise arise largely as a consequence of orderings of non-translational degrees of freedom (see below).

A Multipole and Mean-Field Description

The large and extremely anharmonic excursions characteristic of the protons in dense hydrogen effectively render the associated electronic problem as one of motion of electrons in an environment with considerable instantaneous disorder. Unlike the problem of electrons moving in an environment established by *phase coherent* harmonic phonons, the electronic structure must necessarily reflect significant incoherence of phase. Thus, instead of a strict long-range coherence of electronic phase normally required, for example, by the geometric phase approach to the determination of electronic polarizability in an extended region (20), a localization by disorder is expected (21), and it will be reinforced by correlation. As has been emphasized by Kohn (22), when strong Coulomb interactions are present, a macroscopic system exhibiting significant overlap of one-electron orbitals can nevertheless possess insulating properties. Even in periodic assemblies of such orbitals there can be disconnectedness of the many-electron wave function, and as noted the presence of disorder (21) can impel this further.

If the zero-point displacements of protons are taken as a measure of departure from a crystalline environment (23), the associated changes in local potential energy for electrons are substantial. Moreover, in a systematic progression from average site to average site, the changes are largely incoherent (and almost completely random in phase I, the rotational phase). This is readily appreciated by noting that the single-particle wave

function can be written in the form $C \exp(i\Phi(\vec{r}, t))$, where the general phase Φ becomes Hamilton's principal function ($W = \hbar\Phi$) in the near classical limit. The momentum of a particle, ∇W , and hence the trajectory, is orthogonal to surfaces of constant W . Since the librational excursions already amount to a considerable fraction of a radian (17), it follows that the classical paths must be tortuous, and hence the phase changes between sites must also be considerable. It also follows that although $\langle \hat{\rho}_p^{(1)}(\mathbf{r}) \rangle$ is periodic, the requisite average is clearly over proton time scales; on electronic time scales the problem presented embodies one of considerable disorder, as noted. Now add to this the additional disorder expected when densities are such that proton exchange accompanying tunneling ensues (24). The possibility of extending the notion of localization-by-disorder of electrons to quite considerable densities also then ensues.

In an independent electron picture the problem can therefore be viewed as one admitting of disorder that is principally site-diagonal, and this can lead to localized states separated from itinerant by a mobility edge (21). The envelopes of the states, considered localized, will decay exponentially and will not conform to the Bloch character expected for states in a truly periodic system. On restoring interactions in the many-electron problem disconnectedness is expected in the wave function and because of this (and in spite of a relatively wide spectrum of electron states) it suggests that a continued multipole expansion approach may be valid. However, the incoherence of proton motion necessarily implies a site dependence of the coefficients of such an expansion, and in a first approximation this will be averaged out. The essential difference from the one atmosphere or low density situation is that the associated expansion coefficients must also acquire through this averaging a state dependence, most prominently upon density if temperatures are low. As will be seen below, this viewpoint is largely corroborated by the molecular-field argument to follow, which will be seen to reasonably well reproduce the key experimental features of the phase II–phase III fragment of the phase diagram.

The suggestion put forth in ref. 17 on the possible appearance of a charge ordered broken symmetry crystalline state were based on the results of *ab initio* density functional calculations, but restricted to the ground state and to static protons. For the dynamic case the notion of the development of charge asymmetry is being extended in an average sense to the localized charge. We may also progress to a somewhat wider region of the phase diagram depicted in Fig. 1 using the mean-field approach and the same hypothesis of electronic charge localized by disorder within appropriate boundaries; further, we can also examine the isotopic dependence of these phase boundaries of particular interest is the region of confluence of the lines separating phases I, II, and III (near the triple point).

Vibron and libron timescales differ by about an order of magnitude, so the primary assumption being made is equivalent to the assertion that the fast (vibron) degrees of freedom have been traced out in pursuit of an effective Hamiltonian governing the motion of the slower degrees of freedom (rotational or libron). Under conditions where the phases are close to confluence, the acoustic phonons have frequencies which, in large measure, are also in excess of the libron frequencies. A similar argument can therefore be made for these though with somewhat less force. On the basis of the foregoing the requisite Hamiltonian is then argued to have a largely multipole character, and its form follows from first taking an electronic trace of the fundamental Hamiltonian Eq. 5 or Eq. 7. For much of the phase diagram of Fig. 1, experiment has certainly established that the electronic trace of Eq. 5 leads to a state that can be described as quite weakly coupled “molecules,” these assuredly leading to at least quadrupolar coupling. More accurately these four-particle ($2e + 2p$) units have correspondingly well defined internal physics resulting, for example, in an anisotropic polarizability.

In a frame in which the proton-pair axis is aligned along \hat{z} the polarizability tensor has component $\alpha_{xx} = \alpha_{yy} = \alpha_{\perp}$ and $\alpha_{zz} = \alpha_{\parallel}$ (the others vanishing by symmetry). To set a scale, for the free molecule $\alpha_{\parallel} = 6.76a_o^3$ and $\alpha_{\perp} = 4.74a_o^3$; for later use it is important to note that α_{\parallel} significantly exceeds the average polarizability $\langle \alpha \rangle = 5.6a_o^3$. Accordingly, we might reasonably begin with a lattice of *effective* molecules that interact primarily through quadrupolar terms. However, as noted the analysis of ref. 17 predicts that beyond a certain density, and for certain structures, hydrogen can adopt a state of spontaneous polarization, and in treating an electronic trace of Eq. 5 we must necessarily permit the possibility of emerging dipolar interactions as indicated above; these are also expected to be significant functions of state, here mainly of density.

To establish a *mean-field* Hamiltonian for quadrupolar (and eventually also dipolar) interactions, we therefore first invoke an adiabatic separation of time scales and for instantaneously fixed proton coordinates we take the electronic trace of Eq. 5, the result being used as a Hamiltonian to determine the succeeding proton motion. Two very different physical situations can be imagined according to choice of density (r_s); first, that the electron trace is carried out over states with no symmetry breaking (the familiar quadrupolar case at lowest order). The second, and here the notion of a time average location (the minimizing “structure”) of the protons is crucial, arises from a trace over electronic states that display a time average broken symmetry, to be associated with a spontaneous polarization and hence to the appearance of dipolar terms. Accordingly, let an *emerging* dipole moment be denoted by $\hat{\mathbf{d}}_i$ and let Q_i be the $\ell = 2, m = 0$ component of the permanent quadrupole moment. The entire instantaneous assembly $\{\hat{Q}_i\}, \{\hat{\mathbf{d}}_i\}$ of quadrupoles and dipoles must obviously give rise to a site-dependent field. In the language of mean-field theory a single proton pair can be said to find itself in an average field $\mathbf{E}(\langle \hat{Q}_i \rangle, \langle \hat{\mathbf{d}}_i \rangle)$ arising from *all other* proton pairs, i . Given this, a straight-forward approach immediately suggests itself; we simply determine the requisite averages $\langle \hat{Q}_i \rangle$, and $\langle \hat{\mathbf{d}}_i \rangle$ for the chosen pair from statistical mechanics, these contributing to the determination of the mean-field itself, and then iterate the procedure to self-consistency.

It is unnecessary to assume that all dipoles have identical directions of polarization. However, we do assume that all pairs possess identical *magnitudes* of polarization, this being consistent with symmetry constraints imposed by the crystalline spatial structure. In ref. 17, two structures ($cm2/m$ and $cmc2_1$) were found to give rise to spontaneous polarization. Two other structures, $p2_1/c$ and $pca2_1$, also permit spontaneous polarization (12, 14) where pairs may be found in symmetrically related sites of the unit cell. The corresponding polarizations are also then related by symmetry and are equivalent in magnitude. For specified periodic lattices of dipoles of identical magnitudes the field at a given site can be determined, as is well known (25). In general this field need *not* be parallel to the chosen molecular axis; indeed, it is even possible for it to be antiparallel to the assumed net direction of polarization. However, configurations for which the field constructively reinforces the polarization have been found to be energetically most favorable in the hydrogen problem, and these will be assumed here.

Low Temperature and High Pressure Phases

Given that the scale of density is being represented by the linear measure r_s , it follows that quadrupole–quadrupole energies will scale as r_s^{-5} , dipole–dipole as r_s^{-3} , and quadrupole–dipole (and dipole–quadrupole) as r_s^{-4} . If \hat{L} is the angular momentum operator for a proton pair with principal moment of inertia I , then within the effective molecule picture (and to within volume dependent terms largely originating with the electronic Hamiltonian) the reduced Hamiltonian we consider is now readily seen to be

$$\hat{H} = \hat{L}^2/2I + (E_{qq}/r_s^5)\langle \hat{Q} \rangle \hat{Q} + (E_{dd}/r_s^3)\langle \hat{\mathbf{d}} \rangle \hat{\mathbf{d}} + (E_{qd}/r_s^4)\langle \hat{Q} \rangle \hat{\mathbf{d}} + (E_{dq}/r_s^4)\langle \hat{\mathbf{d}} \rangle \hat{Q} + d_{\parallel}^2/2\alpha_{\parallel} + d_{\perp}^2/2\alpha_{\perp}. \quad [8]$$

Observe that the symmetry of Eq. 8 is strictly appropriate only for structures in which any ensuing order possesses an axis of threefold symmetry through the pairs; examples are *hcp-c*, where pair axes are aligned along the *c* axis, and *Pa3*. A lowering of the corresponding symmetries introduces additional axial anisotropy in a way that the components Q_{xx} and Q_{yy} of the quadrupolar tensor may no longer be strictly equal. This can lead to further nonvanishing components $\langle \vec{Q}_{2,m} \rangle$ ($m = \pm 2$) that may favor additional axial anisotropy in the eventual ordering. In the context of the mean field treatment that now follows, the effects of these will be taken to be subsumed in the mean field itself, but it should be noted that the Landau free energy that corresponds to Eq. 8 possesses terms of all orders (including third) even when the higher symmetry is incorporated.

The values of the state-dependent couplings $E_{\bar{q}q}$, $E_{\bar{a}d}$, $E_{\bar{d}q}$, and $E_{\bar{q}d}$ will initially be taken in a range reasonably close to those appropriate to the free molecule values of the quadrupole moment and polarizabilities, and the respective couplings between them are those expected from classical interacting multipoles. A large negative value for $E_{\bar{q}q}$ clearly implies that the quadrupolar couplings will strongly favor orientational ordering ($\langle \vec{Q} \rangle > 0$) along some assumed direction. On the other hand, the setting of $E_{\bar{q}d} = 0$ will certainly indicate that the quadrupole field at a lattice site vanishes, something which will automatically follow if the center of the proton pair coincides with a site possessing inversion symmetry. If the pairs should eventually be polarized then there is an irreducible energy cost to establish them and this must be recouped from the long-range energy in any eventual stable state of spontaneous polarization (25). The last two terms in Eq. 8 represent this energy penalty (here d_{\parallel} and d_{\perp} are simply the components of the emerging dipole moment parallel and perpendicular to the pair axis, respectively). If \mathbf{E} is the local field at a given pair (here interpreted as the *mean field*) then with sufficient accuracy we may take $\hat{\mathbf{d}}$ as given by linear response ($\hat{\mathbf{d}} = \vec{\alpha} \cdot \mathbf{E}$). As a consequence it follows that for an arbitrary orientation of a given pair with respect to \mathbf{E} we may first solve for $\hat{\mathbf{d}}$ in a frame in which $\vec{\alpha}$ is diagonal and then simply rotate back to the frame in which \mathbf{E} is along \hat{z} . For $\mathbf{E} = E_o \hat{z}$ this gives

$$\hat{\mathbf{d}} = E_o \{ (\alpha_{\parallel} - \alpha_{\perp}) \cos \phi \sin \theta \cos \theta, \\ (\alpha_{\parallel} - \alpha_{\perp}) \sin \phi \sin \theta \cos \theta, \alpha_{\parallel} \cos^2 \theta + \alpha_{\perp} \sin^2 \theta \}, \quad [9]$$

where θ and ϕ define the orientation of the dipole with respect to the field. It is clear that if long range dipole–dipole interaction energies attain levels exceeding the penalty of forming a dipole (of order $d^2/2\alpha$), then it is obligatory to go beyond linear response (for otherwise the dipoles themselves can diverge). Given the symmetry of this problem, the next term in energy cost will be of the form $(b/4)d^4$ so that the energy of a polarizable pair in a local field \mathbf{E} is now $-\mathbf{E} \cdot \hat{\mathbf{d}} + d^2/2\alpha + (b/4)d^4$. We have found that the results for spontaneous polarization are *not* sensitive to b ; an increase in b by a factor n leads to a decrease in d by only a factor of $1/n^{1/4}$, for constant energy cost.

We are evidently drawn towards structures in which pairs align along the direction of \mathbf{E} and for which both dipolar and quadrupolar interactions act constructively. Other arrangements are certainly possible but in energetic terms less favorable, and they do not correspond to the structures found by *ab initio* methods at low temperatures (12–14). In a frame in which a pair aligns, the expectation value of the Cartesian quadrupole moment tensor is diagonal; it follows that $\langle Y_{2,\pm 1} \rangle = 0$. Since the \hat{x} and \hat{y} components of $\hat{\mathbf{d}}$ in Eq. 3 are sums of $Y_{2,\pm 1}$, only the \hat{z} component possesses a nonvanishing expectation value. Accordingly we may now write

$$\langle \hat{\mathbf{d}} \rangle = E_o \{ 0, 0, \alpha_{\parallel} \langle \cos^2 \theta \rangle + \alpha_{\perp} \langle \sin^2 \theta \rangle \} \quad [10]$$

in place of Eq. 9; here, $\sin^2 \theta = (2/3)[1 - 4\pi/5Y_{2,0}]$. Given this we can immediately solve for $\langle \hat{\mathbf{d}} \rangle$ when a trial pair wave function is specified for the requisite averages in Eq. 8.

The states of Eq. 8 are readily obtained by adopting for such a trial wave function a linear combination of spherical harmonics. This approach has been successfully used for other quantum rotor systems, for example, diatomic solids and solid methane, and it has also been applied to the ground state of solid hydrogen (26–32) at lower pressures. We therefore proceed with an initial specification of the field parameters $E_{\bar{q}q}$, $E_{\bar{a}d}$, $E_{\bar{d}q}$, and $E_{\bar{q}d}$, all of which eventually depend on the structure, and of the density r_s (which for a given temperature may be converted via the equation of state to a pressure p). The Hamiltonian Eq. 8 is then diagonalized using a basis set $\{Y_{\ell m}\}$, for a given choice of ℓ_{\max} . The choice of *even* values for ℓ_{\max} , corresponding to para- H_2 or ortho- D_2 has a significant effect on the transition between phases I and II, but in fact rather little effect on the transition between phases II and III; here we shall illustrate the procedures with H_2 . The choice $\ell_{\max} = 2$ give results that already differ very little from the choice $\ell_{\max} = 4$ when conditions close to the order-to-disorder transition are specified (where $\langle \vec{Q} \rangle$ is also already small).

Once the Hamiltonian Eq. 8 is diagonalized and the corresponding states are obtained, an *average* order parameter, for example $\langle \vec{Q} \rangle$, is easily found at a given temperature according to the standard canonical prescription

$$\langle \vec{Q} \rangle = \text{Tr}(\vec{Q} e^{-\hat{H}/\kappa_B T}) / \text{Tr}(e^{-\hat{H}/\kappa_B T}),$$

and then $\langle \hat{\mathbf{d}} \rangle$, also now a function of temperature for a given density, follows immediately from Eq. 10. This leads to a new value of the mean field and hence to a new Hamiltonian (8). For a given r_s and T the entire procedure is then iterated to self-consistency as noted above (and in practice the procedure is rapid). The state eventually arrived at could in principle be *metastable*, and to ensure that it is not, the procedure must be repeated with initial choices of $\langle \vec{Q} \rangle$ and $\langle \hat{\mathbf{d}} \rangle$ both set equal to zero, and also to values greater than zero (four possibilities) with a comparison then being made of the corresponding free energies. For most of the region of the phase diagram to be presented the states are by this means determined to be stable.

Some features of the approach just described bear a resemblance to treatments of the classical Maier–Saupe model for classical quadrupolar ordering (33, 34) as has already been noted by Mazin *et al.* (35); the difference here is that the quadrupoles may also be coupled to an *effective* spin-1 Ising model (36) (and, of course, the approach clearly proceeds from quantum mechanics). The method followed above is actually more complex, because *two* orderings are coupled (those corresponding to $\hat{\mathbf{d}}$ and to \vec{Q}). Nevertheless the similarities do suggest distinct possibilities for the emergent phase diagram of dense hydrogen. When coupling to external fields are present (an interesting experimental point in principle for what follows) the transition can become continuous (33).

A term equivalent to an external field can physically arise if the proton pairs undergo a transition to a state of self-sustaining polarization, as both experiments and theories suggest. Should this be the case then they can be taken to establish an effective “external” field (16) for a system of quantum quadrupoles. In fact, this may not actually occur in hydrogen, the physical reason being traced to the considerable *anisotropy* of the proton-pair polarizability alluded to earlier. Because of this it becomes far more difficult to polarize hydrogen when the pairs are *not* orientationally ordered. The polarizing field is required to be much smaller simply because the average polarizability ($\vec{\alpha}$) is significantly lower than α_{\parallel} . When the pairs orientationally order, the field required to polarize them can then be considerably weaker and they can more easily polarize in a self-sustaining manner. Given this it is expected that

the transition to orientational order ($\langle \hat{Q} \rangle > 0$) will remain first order, though perhaps not prominently.

The phase diagram for the spin-1 Ising model is quite complex; it is expected that the phase diagram for Hamiltonian Eq. 8 may also exhibit a similar richness of detail. For the dipolar terms in Eq. 8 the cost of forming the dipoles is initially proportional to at least d^2 , as already noted. In phase III this is self consistently compensated by the aggregate of long-range dipole–dipole interactions, and also the coupling of the dipoles to the quadrupole fields when $\langle \hat{Q} \rangle \neq 0$. As stated earlier, the range of parameters ($E_{\bar{q}q}$, etc.) is limited to values typical for hydrogen under the conditions of compression appropriate to Fig. 1.

Results and Isotopic Dependence

Experimentally there are significant isotope effects; for example, D_2 orders from phase I to phase II at a notably lower pressure than does H_2 , and this may be traced in part to the larger mass leading to a lower orientational zero-point energy in Eq. 8. In addition, within a few GPa the low temperature transition from phase II to phase III occurs at $p \sim 150$ GPa for both H_2 and D_2 . Put another way, for dense hydrogen and deuterium, whose dynamics differ considerably, this transition is nevertheless occurring at essentially the same densities. Finally, the $(2e + 2p)$ units appear ordered ($\langle \hat{Q} \rangle \neq 0$) in both phase II and phase III, but the experimental evidence suggests a far higher (and state dependent) degree of polarization in phase III. Finally, it appears from the measurements that the transitions may be first order.

A very plausible possibility now arises given the form of Eq. 8: it is that in both phase II and phase III the basic underlying configurations of the proton pairs are physically similar and that, as adduced above, the transition to phase III represents a fundamental change in *electronic order*, one that is being manifested by the presence of state-dependent average dipoles. In classical terms the transition takes place at a density where for a favorable structure the aggregate of the dipole–dipole interactions become sufficient to account for the $\sim d^2/2\alpha$ penalty (here d is a characteristic dipole moment and α is now an average polarizability). For this to happen, $E_{\bar{q}q}$ must be sufficiently large (and negative) to account for the quadrupolar ordering, and $E_{\bar{d}d}$ must also be sufficiently large in order that the molecules may self-consistently polarize. The term $E_{\bar{q}d}$ may or may not be zero, indicating thereby whether (or not) there is a quadrupole field weakly polarizing the molecules in phase II.

First, take $E_{\bar{q}d} = 0$. For this case, the molecules participate in a first-order transition, as expected, and in fact no polarization is found in phase II (23). But as noted, if the density is increased sufficiently the molecules may indeed self-consistently polarize, leading to a large increase in $\langle \hat{d} \rangle$; this is found. The change in polarization, though sharp, is continuous (23). The parameters used in this calculation are (all units are atomic, e.g. $e^2/a_0 = 27.2$ eV) $E_{\bar{q}q} = -0.155$, $E_{\bar{q}d} = 0$, $E_{\bar{d}d} = 0.5$, and $E_{\bar{d}q} = 0$, choices that lead to strong quadrupole–quadrupole and dipole–dipole ordering. Although this model does *not* agree with observation (for as noted, the transition to phase III appears to be first order), it may be mentioned that it *does* give qualitative agreement with the I–II phase boundary, particularly the observed isotope dependence. This behavior simply reflects quadrupole ordering and it implies that quadrupole ordering alone actually *does* provide a reasonably semiquantitative explanation for the I–II phase boundary. Referring to Fig. 2, it can be seen that the transitions for both isotopes are actually first order at this level.

Second, consider the case $E_{\bar{q}d} \neq 0$. For small values of $E_{\bar{q}d}$, it is found that the molecules can self-consistently order in a first-order transition, and actually the results are quite similar to those presented above, but with the anticipated difference that there is now a weak polarization arising from coupling to a quadrupolar field in phase II. The transition to the polarized state (phase III) is continuous but once again, this model does *not* completely agree with observation. Of the two, the choice,

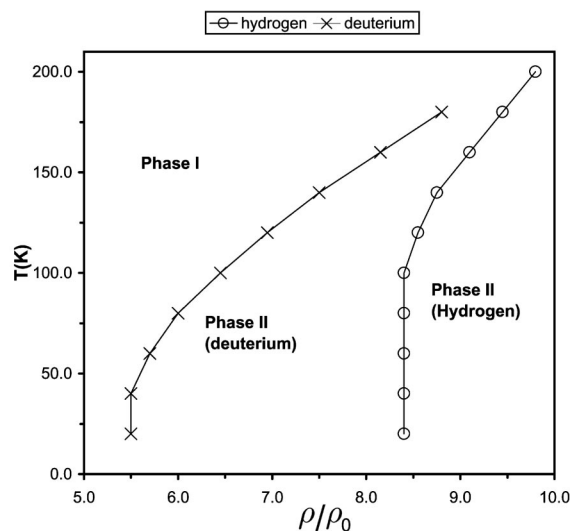


Fig. 2. Phase diagram corresponding to $E_{\bar{q}q} = 0.155$ and all other field parameters set to zero. This purely quadrupolar ordering is already in reasonable agreement with the phase I–phase II boundary.

$E_{\bar{q}d} \neq 0$ gives better agreement in that weak polarization is certainly observed in phase II.

Accordingly, we eventually are led to a model in which the quadrupole–quadrupole coupling is *weaker* than proposed above, but the dipole–dipole coupling is *stronger*. This can result in just a single phase transition, but both $\langle \hat{Q} \rangle$ and $\langle \hat{d} \rangle$ proceed from zero to nonzero across the same phase boundary. That is, the molecules order orientationally but as they do they simultaneously polarize; this correspondence arises from the difficulty (referred to above) in self-consistently polarizing the molecules when they are *disordered*. But once they order, this difficulty is obviated and a confluence of ordering and polarization may occur. Here *both* $\langle \hat{Q} \rangle$ and $\langle \hat{d} \rangle$ transitions are first order, quite in agreement with experiment. The parameters in this calculation are $E_{\bar{q}q} = -0.062$, $E_{\bar{d}q} = 0$, $E_{\bar{d}d} = -0.65$, and $E_{\bar{q}d} = 0$, and the difference in densities for the two isotopes is actually *much smaller* than observed in pure quadrupolar ordering (23). Since the polarization (at densities at which self-consistent polarization is energetically favorable for ordered systems, but *not* disordered) helps to *drive* the ordering, it is clear that this electronic contribution is crucial to the experimental similarity in the densities of the II–III phase boundary in hydrogen and deuterium. It therefore cannot be inferred that quadrupoles alone can impel the ordering.

These results suggest that phases II and III may represent two different underlying molecular structures, with phase II assuming a structure very favorable to quadrupolar ordering (such as $p2_1/c$) and phase III then being very favorable to self-consistent polarization (such as $c2/m$). It is not necessary that the II–III boundary represent exactly the situation illustrated above in which $\langle \hat{Q} \rangle$ and $\langle \hat{d} \rangle$ order at precisely the same density in the structure representing phase III. So long as spontaneous polarization in a structure B occurs at a density less than the density of the transition to phase III, but spontaneous polarization in a structure A only occurs at densities greater than that of the transition, then there will be a discontinuous increase in $\langle \hat{d} \rangle$ at the transition from A to B at such a density (the system will go from a situation in which spontaneous polarization is not energetically favorable to one in which it is, not just by increase in density, but by changing structure).

A phase diagram for H_2 , with *two* structures, one with very strong quadrupolar ordering ($E_{\bar{q}q} = -0.155$) and one with significant quadrupolar ordering ($E_{\bar{q}q} = -0.127$) and strong dipolar interactions ($E_{\bar{d}d} = -0.548$), is shown in Fig. 3. The

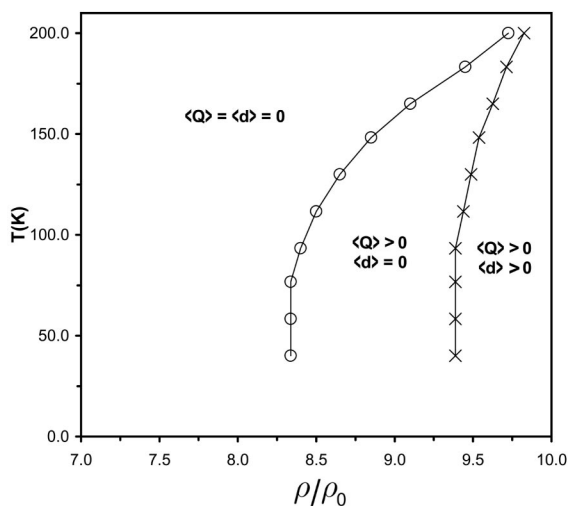


Fig. 3. A possible phase diagram for hydrogen, at low temperatures and with two structures (compare with the experimental summary in Fig. 1): here the parameters of Eq. 8 are (o) $E_{qq} = -0.155$ (x) $E_{qq} = -0.127$ and $E_{dd} = -0.548$. As can be seen, both transitions are of first order.

circles indicate the first-order orientational transition in the system with stronger quadrupolar interactions, which orders at lower pressure but does not polarize ($\langle Q \rangle > 0$, $\langle d \rangle = 0$). To the right of the x's the system is ordered and polarized, in a structure which very strongly favors dipolar interactions. The phase line (represented by the crosses) is also first order. This phase diagram is in very reasonable agreement with respect to its form when compared with the experimental phase diagram of H_2 . Where the two phase lines meet there will be a triple point. All of the transitions are first order, so that within this model there is no tricritical point.

Conclusions

The physical picture that emerges from this approach can be summarized as follows. Phase I represents an orientationally disordered phase within the hexagonal class of structures, as is known. The transition to phase II is well described by an orientational-ordering transition, driven by quadrupole-quadrupole interactions in (8). The structure in phase II is thus

likely to be very favorable to quadrupolar interactions; $Pa3$ and $Pca2_1$ emerge as possible candidates. $Pca2_1$ is among the lowest-energy structures found by *ab initio* calculations for static lattices in the density region corresponding to phase II, so that these calculations and the mean-field analysis above are in agreement. The shape of the phase diagram indicates that the transition to phase III is described by a transition to a spontaneously polarized state, and it is crucial to reemphasize that the transition not only leads to polarization, but is in fact partially driven by polarization. The largely electronic character of this transition helps to explain the near lack of isotope dependence of the transition to phase III from phase II. The antiferroelectric structure $c2/m$ found by using *ab initio* methods is also quite favorable to spontaneous polarization (the dipole-dipole coupling is again very strong). Thus the progression suggested by these results is that phase I-phase II-phase III corresponds to *hcp* (orientationally disordered) $-Pca2_1 - c2/m$. Though the detailed shapes of the phase boundaries determined in the above can clearly be improved, the general agreement they bear to the experimental boundaries suggests that this underlying physical picture has some validity. Experimental determination of the actual structure of phase III would benefit these calculations considerably, particularly in the final assignment of parameters.

Eventually the picture presented here must break down upon sufficient increase in density, the expected closure of the gap signalling one obvious limit. An important guide to the persistence of the multipole character of the charge distribution can certainly be gained by further experimental pursuit of the infrared activity in phase III. In particular, such studies may have much to say about the tunneling phase discussed above, which may well presage the onset of a pressure induced ground-state liquid (37, 38). The physical expectation has long been that the paired structure will give way to a monatomic system at sufficiently high densification *en passant* an insulator to metal transition. Close to pair destruction vibrational/continuum Feshbach resonances may be expected, and in the metallic state that has formed, the consequences of these on the electronic pairing problem (and consequent high temperature superconductivity) may be very considerable indeed (N.W.A., unpublished work).

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