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Energetics of Ordered Structures in Molecular Hydrogen.

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PACS. 61.50K – Crystallographic aspects of polymorphic and order-disorder transformations.
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Abstract. – The energetics of ordered structures in molecular solid hydrogen under high pressure are studied through first-principles calculations. It is found that structures with the molecular axes lying close to the (a, b)-plane of a hexagonal close-packed lattice have in general lower energy and wider band gaps. Coherent rotation of tilted molecules around the c-axis is shown to be almost free. A new lowest-energy geometry is identified in which molecules in alternate planes are antiparallel. Possible superstructure arrangements are discussed.

At moderate to high pressure hydrogen forms a molecular solid which exhibits intriguing behavior. The solid has an overall hexagonal close-packed (h.c.p.) lattice structure at low pressure, but individual molecules undergo large rotational motion which persists up to extremely high pressures, beyond 150 GPa (1.5 Mbar) [1, 2]. A transition to an atomic phase is expected at very high density when the inter- and intramolecular distances become comparable [3, 4]. In contrast to the molecular phase, which at low pressure is a wide-gap insulator, the atomic phase is expected to be metallic [5]. The band gap of the molecular phase decreases almost linearly with increasing density [6]. If the molecular phase were to retain a nonvanishing band gap up to when it transforms to an atomic metallic phase, this transformation would be linked to a metal-insulator transition. Recent diamond anvil cell experiments have discovered that a transition apparently takes place *within* the molecular phase and is signaled by a discontinuity in the intermolecular vibration frequency (vibron discontinuity) [7]. This transition has been linked to the onset of metallic behavior by gap closure in an ordered molecular structure [6, 8-10]. However, the presence or absence of a band gap in the electronic spectrum is very sensitive to the relative orientation of molecules in the h.c.p. lattice [11]. It is crucial therefore to establish which structures are energetically favored in the range of densities near the vibron discontinuity, and whether these structures can account for the observed behavior.

The aim of this letter is to examine the energetics of different molecular orientations and establish general features that prevail at high density. Our calculations are based on the density functional theory [12] (DFT) and employ the local density approximation (LDA) for the exchange and correlation functional as parametrized by Perdew and Zunger [13] to reproduce the exact results of Ceperley and Alder [14] on the uniform electron gas. The

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Coulomb potential of protons, a large basis of plane waves with kinetic energy up to 52 Ry, and a set of 30 points in the irreducible Brillouin zone were used in the calculations. From convergence studies we have found that these computational parameters give an uncertainty in total energy differences of ± 10 meV per h.c.p. unit cell. We have examined the behavior of the energy as a function of molecular orientation at various densities ranging from 0.31 to 0.48 H/Å^3 or volumes of 3.885 to 2.509 cm^3/mol which correspond to *average* electronic densities of $r_s = 1.732$ to 1.497 a.u. For comparison, solid hydrogen under no external pressures has a density of 0.0524 H/Å^3 or a volume of 23.0 cm^3/mol which corresponds to an average electronic density of $r_s = 3.133$ a.u. The upper limit of the density we have considered corresponds approximately to the vibron discontinuity pressure, if the experimental equation of state is used [15]. Of course, in this range of densities the electronic charge distribution is highly nonuniform, with most of the charge residing between the pairs of protons that form molecules [6].

One weakness of the approach used here is the underestimate of the band gap typical of DFT-LDA calculations, which can affect the comparison of total energies when, at a given density, some of the molecular orientations have no band gap while others remain insulating. For this reason we will discuss here the results for densities at which all orientations have nonvanishing band gap. This allows for a consistent comparison of relative energies but restricts the range of densities to an upper limit of 0.393 H/Å^3, at which point some configurations begin to exhibit gap closure. Our results up to this density indicate that configurations with the molecular axes lying close to the (a, b)-plane of the h.c.p. lattice have in general lower energy and wider band gaps. This behavior is enhanced with increasing density while the system remains insulating. For clarity, we shall illustrate this behavior at a single density.

In fig. 1 and 2 we show the behavior of the total energy and the band gap as a function of

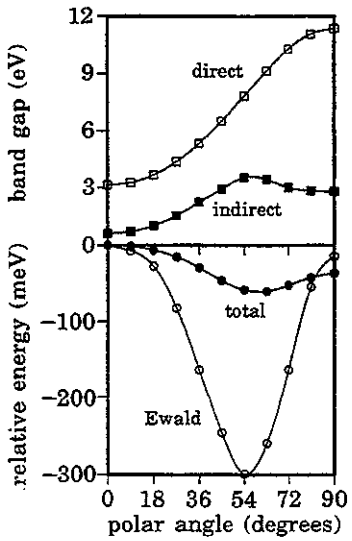

Fig. 1.

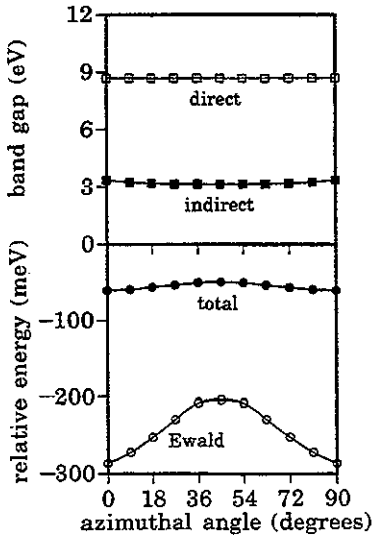

Fig. 2.

Fig. 1. – Relative total and Ewald energies (per h.c.p. unit cell), indirect and direct (at Γ) band gaps as a function of polar angle $\theta = \theta_1 = \theta_2$ for the structure with $\Delta\phi_{12} = 60°$. The zero of energy is defined by the structure with $\theta = 0°$.

Fig. 2. – Same as in fig. 1, for variation of the azimuthal angle ϕ_1, with polar angles fixed at $\theta_1 = \theta_2 = 60°$ and $\Delta\phi_{12} = 60°$.

relative orientation. The results in fig. 1 and 2 correspond to a density of 0.365 H/Å^3. In these comparisons all bond lengths are held fixed constant at 1.40 a.u. (the experimental value in free hydrogen molecules), and the c/a ratio is equal to 1.633, the value in ideal h.c.p. lattices. Four angles are needed to specify the exact position of the two molecules in the h.c.p. unit cell. These are the two polar angles θ_1 and θ_2 that specify the deviation of the molecular bonds from the c-axis of the h.c.p. lattice, and the two azimuthal angles ϕ_1 and ϕ_2 that specify the projections of the molecular bonds on the (a, b)-plane. For symmetry, in all the configurations discussed here we will take the polar angles of the two molecules in each unit cell to be equal ($\theta_1 = \theta_2 = \theta$). We have also considered configurations with $\theta_1 \neq \theta_2$ but these have higher energy than symmetric configurations. In the example of fig. 1 the azimuthal angles are taken to be $\phi_1 = 30°$ and $\phi_2 = 90°$, with the x-axis lying along one translational vector of the (a, b)-plane. This choice of azimuthal angles puts the molecular bonds on planes that bisect the angles between basal translational vectors and gives a difference $\Delta\phi_{12} = |\phi_1 - \phi_2| = 60°$ for molecules on successive planes. This particular arrangement was suggested earlier as a possible low-energy configuration [16]. It is clear from fig. 1 that departure from the $\theta_1 = \theta_2 = 0$ orientation lowers the energy and increases the indirect band gap. The correlation between the total energy and the indirect band gap is striking. The lowest energy and widest band gap is at $\theta = 60°$.

The direct band gap at Γ is also shown in fig. 1, as well as the Ewald energy, *i.e.* the electrostatic interaction of the protons in a compensating uniform background. The direct band gap shows a monotonic increase with θ. The Ewald energy follows closely the behavior of the total energy but varies over a larger scale, with the Ewald energy minimum at a slightly different polar angle ($\theta = 54°$). Thus, the Ewald energy, which is trivial to evaluate compared to the total energy, can be used as a rough guide in searching for low-energy structures in the insulating phase [17]. The electrostatic interaction between protons is partially shielded by the electronic charge in the intermolecular regions, which explains the difference in scale between the Ewald and the total energy. The relation between Ewald and total energy is expected to break down when electronic charge begins to leak out from the molecular bonds into the intermolecular region. When this effect starts to dominate, the band gap between bonding and antibonding states will vanish and qualitatively new behavior could obtain.

Figure 2 shows the behavior of the same quantities when the azimuthal angles are varied for polar angles fixed at $\theta_1 = \theta_2 = 60°$. Here we vary the azimuthal angles so that $\Delta\phi_{12}$ is kept constant at 60°. Thus, ϕ_1 varies from 30° to 90°, while ϕ_2 varies from 90° to 150°. The variation of azimuthal angles gives very small changes in the total energy and the indirect and direct band gaps. Again, the behavior of the Ewald energy follows closely that of the total energy, but on a different scale. These comparisons establish that the energetically most important orientational parameter in the system is the polar angle.

Having considered in some detail the behavior of a particular $\Delta\phi_{12}$ arrangement as a function of polar and azimuthal angle, we then explored the different possible arrangements while keeping the molecular axes on planes bisecting the angles between basal translational vectors. There are six such possible arrangements, with $\Delta\phi_{12}$ taking the values $n \times 60°$, $n = 0, 1, \ldots, 5$. Two of these are equivalent to two others, namely $(n = 1) \equiv (n = 5)$ and $(n = 2) \equiv (n = 4)$. This leaves four independent arrangements ($n = 0, 1, 2, 3$), which together with the $\theta_1 = \theta_2 = 0°$ configuration are shown in top and side views in fig. 3. The polar angles in configurations *b*) through *e*) are held constant at $\theta_1 = \theta_2 = 60°$, by analogy to the results found for the $\Delta\phi_{12} = 60°$ arrangement (fig. 3*c*)) discussed above (see also fig. 1). Table I contains the relative total and Ewald energies of the various arrangements. The lowest-energy structure found here is that with $\Delta\phi_{12} = 180°$. In this structure, the two molecules in each h.c.p. unit cell lie on the same plane. This is also the case for the structure with

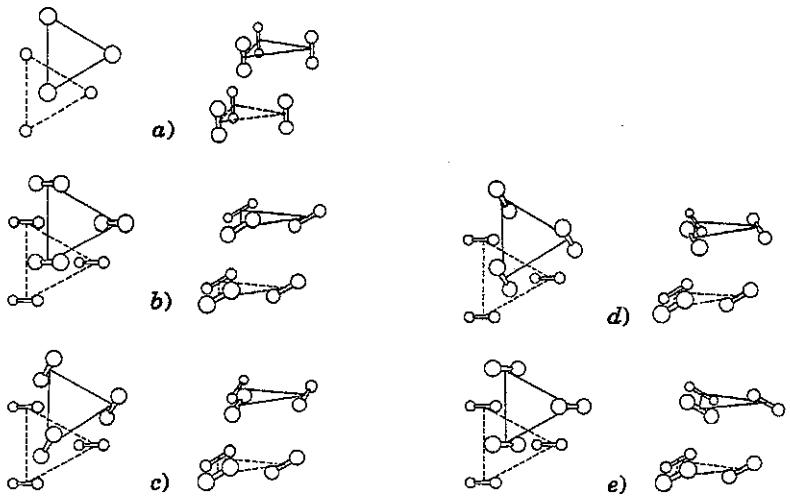

Fig. 3. – Top (along the c-axis) and side (perspective) views of the various molecular arrangements considered. Structure *a*) corresponds to $\theta_1 = \theta_2 = 0°$, structures *b*)-*e*) have $\theta_1 = \theta_2 = 60°$ and correspond to $\Delta\phi_{12} = n \times 60°$, with $n = 0, 1, 2, 3$, respectively. The x-axis that defines $\phi_1 = \phi_2 = 0°$ lies along one of the translational vectors on the (a, b)-plane of the h.c.p. lattice. Three molecules are shown in each plane, and the centres of the molecules in a particular plane are joined by lines for easier identification.

TABLE I. – *Relative total and Ewald energies (in* meV *per* h.c.p. *unit cell) of the various arrangements shown in fig.* 3 *(corresponding labels). The zero of energy is defined by structure a) of fig.* 3, *that is* $\theta_1 = \theta_2 = \phi_1 = \phi_2 = 0°$. *The error bars in total energy come from convergence tests in the calculation (see text).*

Label	$\Delta\phi_{12}$	Total energy (meV)	Ewald energy (meV)
b)	0°	-59 ± 10	-259
c)	60°	-60 ± 10	-286
d)	120°	-75 ± 10	-395
e)	180°	-92 ± 10	-490

$\Delta\phi_{12} = 0°$, but not for the other two arrangements ($\Delta\phi_{12} = 60°$ and $\Delta\phi_{12} = 120°$). In the $\Delta\phi_{12} = 0°$ case the two molecules are parallel. By analogy, the $\Delta\phi_{12} = 180°$ case can be described as having the two molecules antiparallel. (This characterization cannot be applied to configurations with $\theta = 0°$ or 90°, but those structures have higher energy.)

It is interesting to consider the implications of our calculations for the behavior of real solid hydrogen. In the real solid there is large zero-point motion which is extremely difficult to take into account directly in first-principles DFT-LDA calculations. This motion results in bond vibrations as well as rotations and has profound consequences for the behavior of the solid. Our results show that rotation in the azimuthal angle is essentially free, when all molecules move together and the $\Delta\phi_{12}$ parameter is constant (see fig. 2). In contrast, rotation involving changes in polar angle involves large energy barriers (see fig. 1). This suggest that molecules will tend to lie close to the (a, b)-plane, tilted approximately 60° away from the c-axis. Coherent rotational motion of many molecules over several unit cells should be relatively easy, provided their axes maintain the proper tilt. This type of structure would also have less resistance to decreasing the c/a ratio with increasing density, a fact that is consistent with experimental observations [1].

The antiparallel orientation of molecules on alternate planes suggests an «antiferromagnetic» type of coupling: Although in our calculations the H_2 molecules are not magnetic, one can image a 2D spin associated with each molecule, pointing in the direction of the atom which lies above the (a, b)-plane. With this mapping, the arrangement with $\Delta\phi_{12} = 180°$ corresponds to antiferromagnetic coupling of the spins on alternate planes of the h.c.p. lattice. It will be interesting to explore the possibility of supercell arrangements in which a similar type of coupling could exist *within* each plane, as well as across planes. For instance, assuming an XY spin model, which seems appropriate given the freedom in azimuthal rotations, the antiferromagnetic coupling would introduce superstructures of $\sqrt{3} \times \sqrt{3}$ periodicity in the *planar* vectors, *i.e.* a tripling of the unit cell volume. Support for this type of superstructure comes also from analysis of the wave-vector character of states near band extrema of the 1×1 h.c.p. lattice (this will be discussed in detail elsewhere). Interestingly, a tripling of the unit cell volume was found to be energetically favorable in the atomic hexagonal phase as well [18]. It is possible that the vibron discontinuity is related to order-disorder transitions similar to those in spin models. We emphasize, however, that this simple mapping is probably not adequate to fully describe the system, and it is offered here only as an interesting possibility for further study. Arguments about possible superstructures of a *different* type, namely multiple periodicity along the c-axis, have been discussed by Ashcroft [11], and a phenomenological discussion of the vibron transition in terms of an orientational order parameter has been given by Lorenzana, Silvera and Goettel [10].

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