



PCCP

Dimensional interpolation for metallic hydrogen

| | |
|-------------------------------|---|
| Journal: | <i>Physical Chemistry Chemical Physics</i> |
| Manuscript ID | CP-ART-10-2020-005301.R1 |
| Article Type: | Paper |
| Date Submitted by the Author: | 05-Nov-2020 |
| Complete List of Authors: | Ghosh, Kumar Jang Bahadur; University of Denver Daniel Felix Ritchie School of Engineering & Computer Science, Kais, Sabre; Purdue University, Chemistry Herschbach, Dudley; Harvard University, Department of Chemistry and Chemical Biology |
| | |

SCHOLARONE™
Manuscripts

Cite this: DOI: 00.0000/xxxxxxxxxx

Dimensional interpolation for metallic hydrogen

Kumar J. B. Ghosh,^a Sabre Kais,^b and Dudley R. Herschbach^{c†}Received Date
Accepted Date

DOI: 00.0000/xxxxxxxxxx

We employ a simple and mostly accurate dimensional interpolation formula using dimensional limits $D = 1$ and $D = \infty$ to obtain $D = 3$ ground-state energy of metallic hydrogen. We also present results describing the phase transitions for different symmetries of three-dimensional structure lattices. The interpolation formula not only predicts fairly accurate energies but also predicts a correct functional form of the energy as a function of the lattice parameters. That allows us to calculate different physical quantities such as the bulk modulus, Debye temperature, and critical transition temperature, from the gradient and the curvature of the energy curve as a function of the lattice parameters. These theoretical calculations suggest that metallic hydrogen is a likely candidate for high temperature superconductivity. The dimensional interpolation formula is robust and might be useful to obtain the energies of complex many-body systems.

Keywords: *dimensional interpolation, dimensional scaling, metallic hydrogen, superconductivity, large- D limit, one-dimension.*

1 Introduction

In 1935, Eugene Wigner and H.B. Huntington predicted the metallization of hydrogen¹, a phase of hydrogen that behaves like an electrical conductor. Ever since this has been a major quest for condensed matter physics. In pursuing metallic hydrogen (MH), we have admired many papers, but cite a few dealing with extreme high-pressure experiments^{2–7}. Moreover, MH is a candidate for phase transitions from superconductivity to superfluidity and vice versa under the influence of a magnetic field^{8–10}.

Dimensional scaling offers simple solutions for $D = 1$ and $D \rightarrow \infty$ limits, then often interpolates to obtain useful results for $D = 3$, with accuracy adequate for many areas of chemical physics^{11–21}. Already, the $D \rightarrow \infty$ limit for MH was treated in 1992 by John Loeser²². He employed a Hartree-Fock Hamiltonian that localizes the electrons in a lattice of hydrogen atoms with clamped nuclei for rigid three-dimensional simple cubic (SC), body-centered (BCC), face-centered (FCC) cubic proton-lattices. We shall tune up the $D \rightarrow \infty$ limit and develop the $D = 1$ limit for MH and in-

terpolate to obtain $D = 3$. Recently, we used dimensional interpolation to apply ground-state energies for two, three, and four electron atoms and for ground-state H₂ molecule over a wide range of the internuclear distance R . The results compare well with the standard exact energies obtained from the Full Configuration Interaction²³.

Here we investigate the phase transition for metallic hydrogen using dimensional scaling with the three-dimensional proton lattices: SC, BCC, and FCC. Section 2 describes an interpolation formula for extended systems. Sections 3 and 4 develop a one-electron Hamiltonian for quantum theory of MH in SC, BCC, and FCC lattice with $D \rightarrow \infty$ and $D = 1$ respectively. Section 5 implements the dimensional interpolation to obtain $D = 3$, observes MH and its phase transition. Section 6 uses extrapolation and curve fitting to obtain a functional form of the ground state energy of MH in SC, BCC, FCC lattice as a function of the lattice parameter, R , and investigate the physical properties like bulk modulus, Debye temperature, melting curve, and superconductivity. Section 7 has some prospects.

2 Dimensional interpolation formula for extended systems

For dimensional scaling of atoms and molecules the energy erupts to infinity as $D \rightarrow 1$ and vanishes as $D \rightarrow \infty$. Hence, we adopt scaled units (with hartree atomic units) whereby

^a Department of Electrical and Computer Engineering, University of Denver, Denver, CO, 80210, USA; E-mail: jb.ghosh@outlook.com

^b Department of Chemistry and Physics, Purdue University, West Lafayette, IN, 47906, USA; E-mail: kais@purdue.edu

^c Department of Chemistry and Chemical Biology, Harvard University, Cambridge MA 02138, USA; E-mail: dherschbach@gmail.com

$E_D = (Z/\beta)^2 \varepsilon_D$ and $\beta = \frac{1}{2}(D-1)$, so the reduced energy ε_D remains finite in both limits. When expressed in a $1/Z$ perturbation expansion, the reduced energy is given by

$$\varepsilon_D = -1 + \varepsilon_D^{(1)} \lambda + \varepsilon_D^{(2)} \lambda^2 + \dots \quad (1)$$

with $\lambda = 1/Z$, where Z is the total nuclear charge of the corresponding atom.

The interpolation for atoms, developed in Ref.²⁰, weights the dimensional limits by $\delta = 1/D$, providing $\delta \varepsilon_1$ and $(1-\delta) \varepsilon_\infty$ in a simple analytic formula

$$\varepsilon_D = \delta \varepsilon_1 + (1-\delta) \varepsilon_\infty + \left[\varepsilon_D^{(1)} - \delta \varepsilon_1^{(1)} - (1-\delta) \varepsilon_\infty^{(1)} \right] \lambda. \quad (2)$$

For a diatomic molecule, a different scaling scheme is used and illustrated. The rescaling of distances is:

$$R \rightarrow \delta R' \text{ for } D \rightarrow 1; R \rightarrow (1-\delta) R' \text{ for } D \rightarrow \infty. \quad (3)$$

An approximation for $D = 3$ (where $R = R'$) emerges:

$$\varepsilon_3(R') = \frac{1}{3} \varepsilon_1 \left(\frac{1}{3} R' \right) + \frac{2}{3} \varepsilon_\infty \left(\frac{2}{3} R' \right), \quad (4)$$

interpolating linearly between the dimensional limits²⁴⁻²⁷.

We keep the structure of the formula same as above for extended systems like metallic hydrogen. We assume the cubic symmetry for the metallic hydrogen in the large D limit and a linear chain of atoms in one dimension. The rescaled distances in different dimension is given by:

$$\text{In } D = 1 : r \rightarrow r'/3 \text{ and } R \rightarrow R'/3; \quad (5a)$$

$$\text{In } D \rightarrow \infty : \rho \rightarrow 2\rho'/3 \text{ and } R \rightarrow 2R'/3. \quad (5b)$$

The coordinates r and ρ are the electronic coordinates, and the parameter R is the spacing between the atomic nuclei (or lattice parameters) in $D = 1$ and $D = \infty$ respectively.

3 Metallic hydrogen at the large- D -limit

With appropriate scaling, energies will be in units of $4/(D-1)^2$ hartrees, and distances in units of $D(D-1)/6$ bohr radii. Loeser applied with simplifications the Hartree-Fock one-electron Hamiltonian in the $D \rightarrow \infty$ limit in a lattice of hydrogen atoms with clamped nuclei²²:

$$\mathcal{H} = \frac{9}{8\rho^2} - \frac{3}{2\rho} + W(\rho, R), \quad (6)$$

where

$$W(\rho, R) = \frac{3}{4} \sum_{\substack{l,m,n \\ \in \mathcal{L}'}} \frac{1}{\sqrt{\sigma^2 R^2}} - \frac{2}{\sqrt{\sigma^2 R^2 + \rho^2}} + \frac{1}{\sqrt{\sigma^2 R^2 + 2\rho^2}}, \quad (7)$$

with

$$\sigma^2 = l^2 + m^2 + n^2, \quad (8)$$

for some set of integer triples l, m, n . In particular, the set of all integer triples gives the SC lattice, the set with l, m, n all even or all odd gives the BCC lattice, and the set with even $l+m+n$ gives the FCC lattice.

For any specified lattice type and scaled lattice constant R , the minimum of Eq. (6) with respect to ρ gives the energy per electron. The whole lattice is three-dimensional, noted \mathcal{L}' minus the one site $(0,0,0)$. The single variable ρ is the orbit radius and R is the lattice spacing. The quantity (ρ/R) is used to characterize the different density regimes.

We began with the simple cubic lattice. In Hartree-Fock approximation of MH the triple sum $W(\rho, R)$ is a kind of Madelung sum. Loeser evaluated $W(\rho, R)$ for the two limiting cases. For the low-density regime ($\rho \ll R$), the sums over integers are taken from the tables of Born and Misra²⁸ and the Hamiltonian of Eq. (6) becomes:

$$\lim_{\rho \ll R} \mathcal{H} = \frac{9}{8\rho^2} - \frac{3}{2\rho} + 3.89157 \left(\frac{3\rho^4}{2R^5} \right). \quad (9)$$

For the high-density regime ($\rho \gg R$), the sum can be replaced by an integral and the Hamiltonian of Eq. (6) becomes:

$$\lim_{\rho \gg R} \mathcal{H} = \frac{9}{8\rho^2} - \frac{3}{2\rho} + 2.17759 \left(\frac{3\rho^2}{2R^3} \right). \quad (10)$$

For the criticality of the metallic hydrogen, we have to find the critical density for which the above Hamiltonian (6) attends the minimum. For calculation-convenience we fix the parameter $R = 1$ and the lattice size to be $(400 \times 400 \times 400)$. Although ideally the number lattice points should be infinitely large, but for calculation our lattice size is sufficient to observe the critical phenomenon. We calculate numerically and display in Fig.1(a) of the above Hamiltonian for a wide range of ρ , from 0.01 to 65, i.e. the density (ρ/R) ranges from 0.01 to 65. From Fig. 1(b), we find that, for $R = 1$, at density $\rho/R = 0.799$ Hamiltonian (6) attends the minimum.

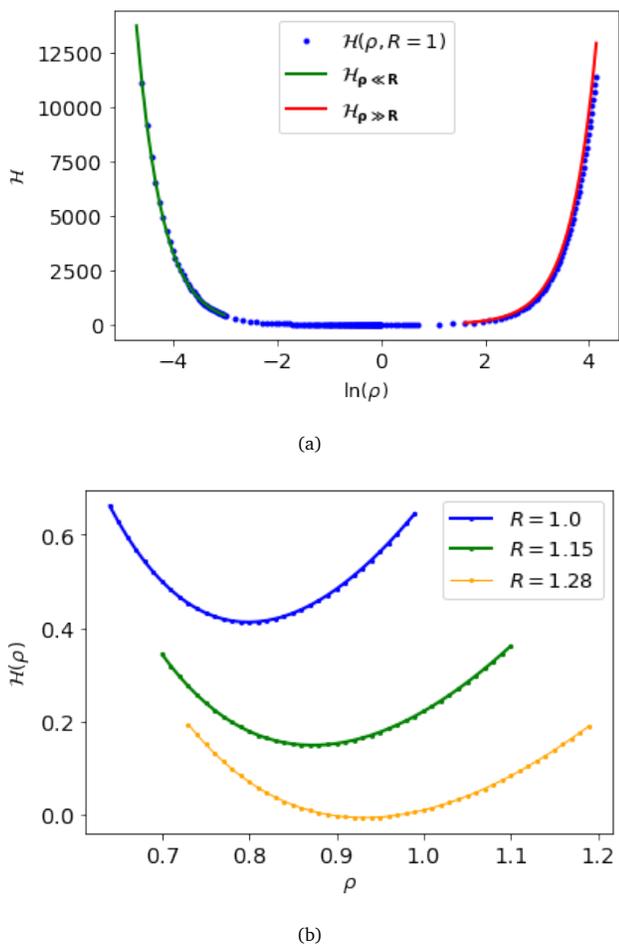


Fig. 1 At the top panel 1(a), we plot the electronic energy per atom $H(\rho, R)$, for MH in SC lattice, as a function of $\ln(\rho)$ keeping the parameter $R = 1$. We also plot the energy for $\rho \gg R$ obtained from Eq.(10) in red, and the energy for $\rho \ll R$ obtained from Eq. (9) in green. At the bottom 1(b), we plot the energy for each atom $\mathcal{H}(\rho)$ as a function of ρ for $R = 1.0, 1.5$ and 1.28 respectively.

Then, we choose different values of R and calculate the minimum of the Hamiltonian $\mathcal{H}(\rho^*, R)$ by varying the parameter ρ for each R , which gives the electronic ground state energy per atom.

At $R = 1.28$, we find $\rho^* = 0.932$ at the minimum and see in Fig. 2(a), the ground state energy becomes positive to negative around $R = 1.28$. Physically this means for $R < 1.28$, the ground state energy becomes positive therefore makes the system is unstable. Therefore, at the point $R = 1.28$ and $\rho^* = 0.932$, the system goes through a phase transition. This is an elemental model at $D \rightarrow \infty$ limit with Hartree-Fock approximation and hydrogen atoms are in a simple cubic lattice, but we observe the criticality and find a critical density for the corresponding critical phenomenon.

Remarkably, Loeser added to the Hartree-Fock approximation in the $D \rightarrow \infty$ limit by introducing inter-electronic

correlation²². That was essentially by opening the dihedral angles in the simple cubic lattice²². As shown in Fig. 2(a), the energy with correlation is nearly the same as without the correlation. Further, in Fig. 2(b), we plot the difference between the correlation energy and the Hartree-Fock energy.

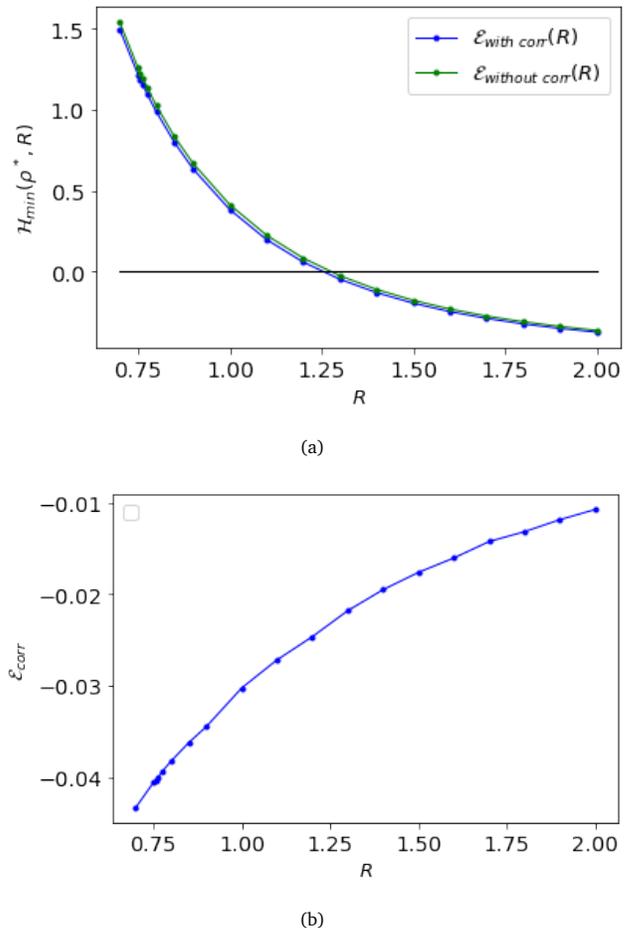


Fig. 2 At the top panel 2(a), we plot the energy obtained at $D \rightarrow \infty$ with inter-electronic correlation in blue, compared with the HF energy as a function of R in green. At the bottom 2(b), the difference between the correlation energy and the HF energy (\mathcal{E}_{corr}) is plotted as a function of R .

We first choose the parameter $R = 1$ in the electronic Hamiltonian per atom and calculate the energies with respect to the variable ρ ; see Fig 3(a). Like the SC case we find a minimum for the Hamiltonian, which is $\rho_{BCC} = 0.88 = \rho_{FCC}$.

Again we calculate the minimum of the Hamiltonian $\mathcal{H}(\rho^*, R)$ for the different values of R by varying the parameter ρ , which gives the electronic ground state energy per atom. From Fig. 3(b), we see that the ground state energy becomes positive to negative around $R = 1.15$ for both FCC and BCC lattices. Hence, the ground state energy

becomes positive so makes the lattice is unstable or the system loses the crystalline structure. Therefore, around the point $R_{BCC} = 1.15 = R_{FCC}$ and the system goes through a phase transition. Since the parameters (ρ, R) at the transition point are same for BCC and FCC lattices, this could be coming from some symmetry working akin to their reciprocal spaces.

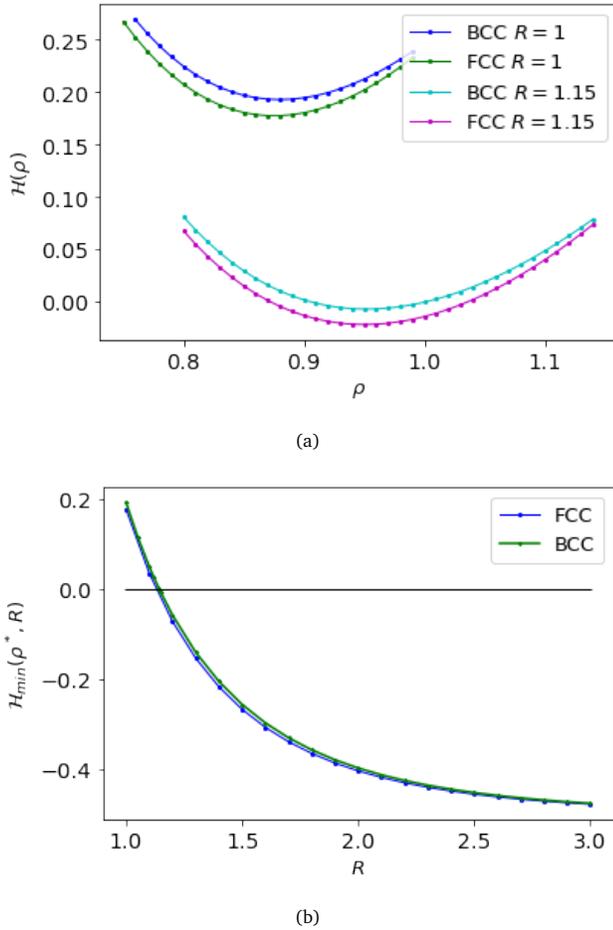


Fig. 3 At the top panel 3(a), we plot the energy per atom $H(\rho, R)$, for MH in BCC and FCC lattices, as a function of the parameter ρ fixing $R = 1$ and 1.15 respectively. At the bottom 3(b), we plot the ground state energy $\mathcal{H}_{min}(\rho^*, R)$ as a function of R .

4 Metallic hydrogen in $D = 1$

A lonely, single hydrogen molecule in one-dimension is described by I. R. Lapidus^{29,30}. However, to investigate the quantum theory of MH in one dimension, we need to develop a long chain of N individual hydrogen atoms, with the nuclei sitting on the lattice sites located at $r = 0, R, 2R, \dots, (N-1)R$. Hence one-electron Hamiltonian in $D = 1$ using atomic units can be written as:

$$\mathcal{H} = -\frac{1}{2} \frac{\partial^2}{\partial r^2} - \sum_{i=0}^{N-1} \delta(r+iR) \quad (11)$$

+ electron-electron interaction part.

We choose the linear combination of atomic orbitals (LCAO) representation and construct the state for each electron in the metallic hydrogen chain in one dimension as follows:

$$\psi(r) = \frac{1}{\mathcal{N}} [\phi_0(r) + \phi_1(r) + \phi_2(r) + \dots], \quad (12)$$

with the of the normalization constant

$$\mathcal{N} = \left[\sum_{i,j} e^{-|i-j|R} (1 + |i-j|R) \right]^{1/2}, \quad (13)$$

and the individual normalized wave functions

$$\phi_i(r) = e^{-|r+iR|}.$$

The kinetic and potential energy part of the above Hamiltonian is calculated as:

$$\begin{aligned} E_{KE+PE} &= \langle \psi(r) | -\frac{1}{2} \frac{\partial^2}{\partial r^2} - \sum_{k=0}^{N-1} \delta(r+kR) | \psi(r) \rangle \\ &= \frac{1}{\mathcal{N}^2} \left[-\frac{1}{2} \sum_{i,j} (-1 + |i-j|R) e^{-|i-j|R} - \sum_{i,j,k} e^{-|i-k|R} e^{-|j-k|R} \right]. \end{aligned} \quad (14)$$

Unlike the nuclei, which are localized at single points, the superpositioned electron-clouds are smeared around the whole lattice. So, to calculate the inter-electronic repulsion part we consider an electron density (or a negative charge density) over an infinitesimally small line element dr at a location r which interacts with another electron density sitting over an infinitesimally small line element dr' at a location r' . The repulsion energy for these two infinitesimally small electron clouds is given by $dE_{ee} = \psi(r)\psi(r)\delta(r-r')\psi(r')\psi(r') drdr'$. Therefore, the total electron-electron interaction part is given by:

$$\begin{aligned} E_{ee} &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} drdr' \psi(r)\psi(r')\delta(r-r')\psi(r)\psi(r') \\ &= \frac{1}{\mathcal{N}^4} \int_{-\infty}^{\infty} dr \sum_{i,j,k,l} \phi_i(r)\phi_j(r)\phi_k(r)\phi_l(r) \\ &= \frac{1}{\mathcal{N}^4} \int_{-\infty}^{\infty} dr \sum_{i,j,k,l} e^{-|r-ir|} e^{-|r-jR|} e^{-|r-kR|} e^{-|r-lR|}. \end{aligned} \quad (15)$$

We break the above expression (15) into many smaller terms and calculate all them individually as follows:

$$\int_{-\infty}^{\infty} dr \phi^4(r) = \frac{1}{2},$$

$$\int_{-\infty}^{\infty} dr \phi_i^2(r) \phi_j^2(r) = e^{-2|i-j|R} \left(\frac{1}{2} + |i-j|R \right), \text{ for } i \neq j,$$

$$\int_{-\infty}^{\infty} dr \phi_i(r) \phi_j^3(r) = \frac{3}{4} e^{-|i-j|R} - \frac{1}{4} e^{-3|i-j|R}, \text{ for } i \neq j,$$

$$\begin{aligned} & \int_{-\infty}^{\infty} dr \phi_i(r) \phi_j^2(r) \phi_k(r) \\ &= \frac{1}{2} e^{(k-i)R} - \frac{1}{4} e^{(3k-i-2j)R} - \frac{1}{4} e^{(2j+k-3i)R}, \text{ for } i > j > k, \end{aligned}$$

$$\begin{aligned} & \int_{-\infty}^{\infty} dr \phi_i(r) \phi_j^2(r) \phi_k(r) \\ &= e^{(i+k-2j)R} \left[\frac{3}{4} + (j-i)R \right] - \frac{1}{4} e^{(3k-i-2j)R}, \text{ for } j > i > k, \end{aligned}$$

$$\begin{aligned} & \int_{-\infty}^{\infty} dr \phi_i(r) \phi_j^2(r) \phi_k(r) \\ &= e^{(2j-k-i)R} \left[\frac{3}{4} + (k-j)R \right] - \frac{1}{4} e^{(2j+k-3i)R}, \text{ for } i > k > j, \end{aligned}$$

$$\begin{aligned} & \int_{-\infty}^{\infty} dr \phi_i(r) \phi_j(r) \phi_k(r) \phi_l(r) = e^{(k+l-i-j)R} [1 + (k+j)R] \\ & - \frac{1}{4} e^{(j+k+l-3i)R} - \frac{1}{4} e^{(3l-i-j-k)R}, \text{ for } i > k > j > l, \end{aligned}$$

and we use the multinomial theorem:

$$(x_1 + x_2 + \dots + x_m)^n = \sum_{k_1+k_2+\dots+k_m=n} \frac{n!}{k_1!k_2!\dots k_m!} \prod_{t=1}^m (x_t)^{k_t}$$

to calculate the interaction part in equation (15).

We set the number of lattice points equal to $i, j, k, l = 100$ and calculate all the above quantities numerically and obtain the final energy as a function of the inter-atomic distance R .

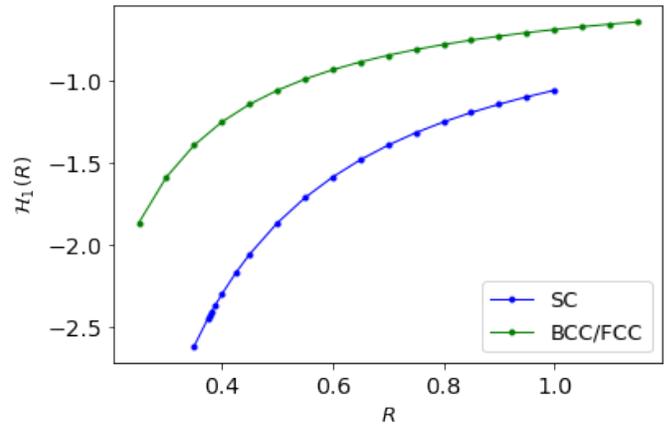


Fig. 4 We plot the energy $\mathcal{H}_1(R)$ for MH at $D = 1$ as a function of R ; blue curve is for SC lattice and green for FCC or BCC lattice.

For FCC or BCC lattices the calculations in $D = 1$ is slightly different from SC lattice in one dimension. For e.g. in case of BCC lattice in $D = \infty$ the Hamiltonian (6), the lattice parameters l, m, n are either even or odd integers²². We choose the same conversion for the calculation in one dimension. In one dimension the FCC and BCC lattices are the same.

For MH in $D = 1$ with inter-electronic correlation there is no way to define dihedral angles between electrons. Therefore, we keep the Hamiltonian same as defined in Eq. (11). In Fig. 4, we plot the energy per electron as a function of the inter-atomic distance R for simple cubic and FCC/BCC lattices.

5 Metallic hydrogen in $D = 3$ from dimensional interpolation

The dimensional interpolation formula described in section 2 combines the $D = 1$ and $D = \infty$ limits and obtains the $D = 3$ reduced energy from

$$\varepsilon_3(R) = \frac{1}{3} \varepsilon_1 \left(\frac{1}{3} R \right) + \frac{2}{3} \varepsilon_\infty \left(\frac{2}{3} R \right). \quad (16)$$

In Fig. 5, we plot the electronic energies involved for the metallic hydrogen in simple cubic lattice (SC). We compare our interpolation $\varepsilon_3(R)$ curve (blue) with points (red) that come from density functional theory³¹ (there Table III). The agreement is very good. As noted in Fig. 2, the inter-electronic correlation examined in the $D \rightarrow \infty$ limit turns quite minor. From Fig. 5 we see that the ground state energy at $D = 3$ becomes positive to negative around $R = 1.14$. Physically this means for $R < 1.14$ the ground state energy becomes positive therefore makes the lattice is unstable or the system loses the crystalline structure. Therefore, at the point $R = 1.14$, the system goes through a phase transition.

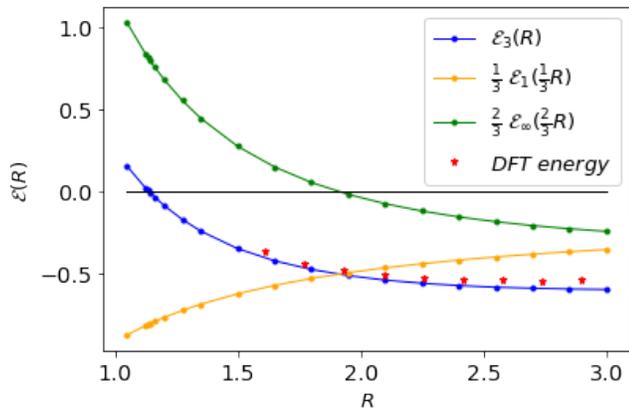
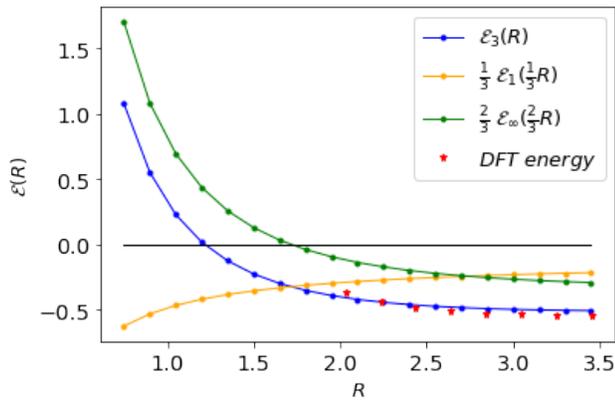
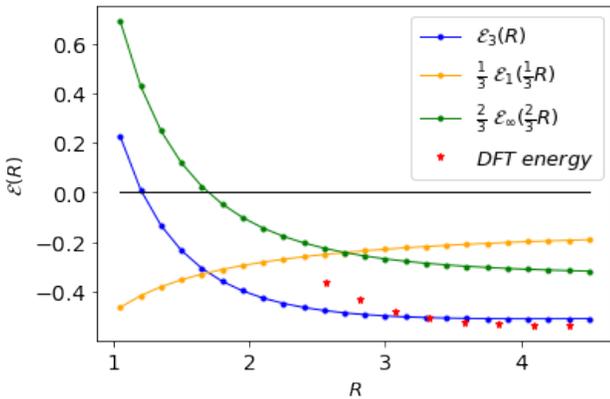


Fig. 5 The orange and green curves describe the results from $D = 1$ and $D \rightarrow \infty$ respectively. The blue curve energy $\mathcal{E}_3(R)$ represented the interpolation result at $D = 3$ for MH, in the SC lattice. The red points represent the results obtained from density functional theory in³¹. The black line shows the zero-energy line, where the blue curve goes through on $R = 1.14$ at a phase transition.



(a)



(b)

Fig. 6 The top panel 6(a) is for the BCC lattice, the bottom panel 6(b) for the FCC lattice. Compare results in Fig. 5 for the SC lattice. Both of the blue curves meet the black line at zero-energy when $R = 1.14$ at the same phase transition for all three lattices

Fig. 6 displays the MH energies from the BCC and FCC lattices, similar to the SC lattice in Fig. 5, interpolating to $D = 3$ from Eq.(16). The corresponding transition point for BCC and FCC lattice, where the ground state energy changes sign, is given by $R_{FCC} = 1.21 = R_{BCC}$.

6 Physical properties of Metallic hydrogen

The scaled lattice constant R is related to r_s , the standard solid state parameter defined as the radius of a sphere (in a_0 bohr units) in which contains on average one electron. For the SC lattice,

$$\frac{4}{3}\pi r_s^3 = R^3. \quad (17)$$

Thus, $r_s = 0.71$ corresponds to the transition point $R = 1.14$, for the $D \rightarrow \infty$ limit. Many studies for $D = 3$ have obtained $r_s = 0.8$ for the existence of crystalline phase of metallic hydrogen³². However, we have simply used R when the interpolation formula provides appropriate energies of metallic hydrogen for different lattice symmetries and parameters.

In this section, we are allowed to calculate different physical quantities such as the bulk modulus, Debye temperature, and critical transition temperature, from the gradient and the curvature of the energy curve as a function of the lattice parameters. Thus, the numerical results of the interpolation formula can be fitted to the following functional form as a function of the lattice parameter R ^{33,34}, driven in a following table and Fig. 7.

$$\mathcal{E}(R) = \frac{A}{R^2} + \frac{B}{R} + C - D \ln(R), \quad (18)$$

with the parameters given in the following table 1 :

Table 1 Parameters describing $\mathcal{E}(R)$ in different lattice structures

| Lattice | A | B | C | D |
|----------------------------------|--------|---------|---------|---------|
| SC in HF limit | 1.3236 | -0.0975 | -0.9650 | -0.2311 |
| SC with correlation ^a | 1.3458 | -0.1689 | -0.9457 | -0.2264 |
| BCC | 0.7889 | 0.7273 | -1.1974 | -0.3397 |
| FCC | 1.1628 | -0.1070 | -0.7329 | -0.1265 |

^a See Fig. 2 has added SC with inter-electronic correlation. Others with Hartree-Fock (HF).

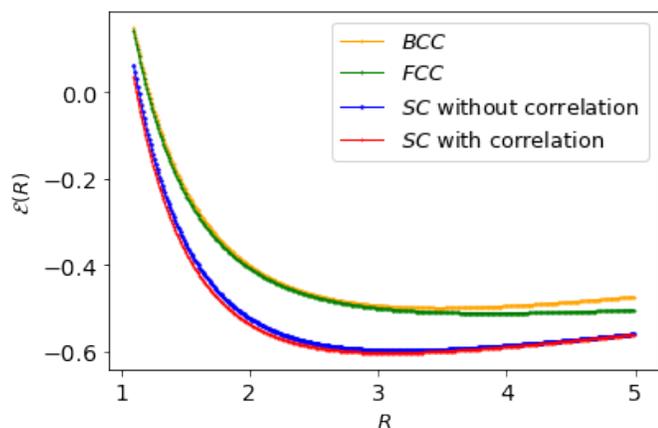


Fig. 7 The simple formula, Eq. (18), fits neatly the energies of MH in Table 1: SC with HF (in blue) and with correlation (in red); BCC (in orange), and FCC (in green) lattice structures respectively.

We also calculate the \mathcal{E}_{min} and R_{min} from Eq. (18) and in Table 2 compare them for the lattice structures:

Table 2 \mathcal{E}_{min} and R_{min} in different lattice structures

| Lattice structure | R_{min} | \mathcal{E}_{min} |
|---------------------|-----------|---------------------|
| SC in HF limit | 3.18 | -0.597 |
| SC with correlation | 3.09 | -0.603 |
| BCC | 3.48 | -0.499 |
| FCC | 3.88 | -0.512 |

The minimum energies of the MH lattices are evident in Fig. 7 and the energy differences are $\Delta_{FCC-SC} = 0.091$, $\Delta_{BCC-SC} = 0.104$, $\Delta_{FCC-BCC} = 0.013$ respectively. The energy differences between FCC and BCC are very modest compared to SC. That may lead to possibility for a phase transition from BCC to FCC structure or vice-versa.

Now we examine briefly consequential properties that involve from the interpolated formula (Eq. 16) for MH energy. First is pressure:

$$P = -\frac{d\mathcal{E}}{dV} = -\frac{\eta}{3R^2} \frac{d\mathcal{E}}{dR}, \quad (19)$$

with η = number of atoms in a unit cell. And we see from the graph that around $R = 3.18$, where $\mathcal{E} = \mathcal{E}_{min}$, the pressure changes sign; the corresponding $r_s = 1.9$. This transition has a physical significance. Although at high densities the crystalline phase is preferred for metallic hydrogen, however at low densities ($r_s > 1.6$) the metallic hydrogen behaves like a fluid or liquid metal^{32,35,36}. This particular point $R = 3.18$ and $\mathcal{E} = -0.597$ possibly signifies that crystalline-fluid transition point for MH in simple cubic lattice.

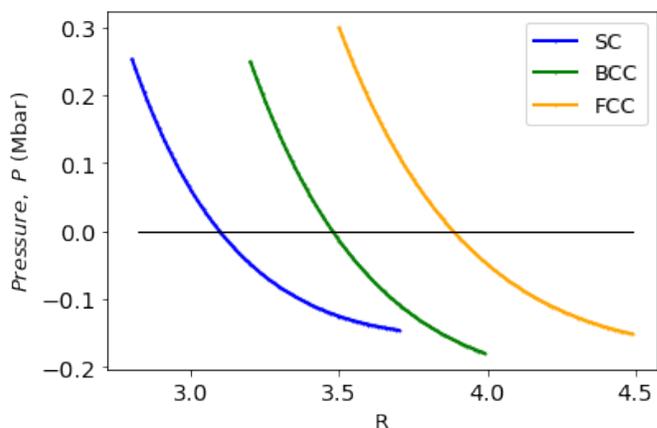


Fig. 8 We plot the pressure P in Mbar for MH in SC (in blue), BCC (in green), and FCC (in orange) lattices as a function of R .

From the curvature of the energy curves in Fig. 7, we can calculate the elastic modulus of MH for different structures as the bulk modulus B of a cubic metallic lattice is given by

$$B = -V \frac{dP}{dV}, \quad (20)$$

with pressure, P , and volume of the unit cell $V = R^3$. The shear modulus G can be calculated from the same equation³⁷. Another important quantity that is available from the MH energy via pressure is the Debye temperature Θ ; the formula^{38,39} involves quite a few items:

$$\Theta = \frac{h}{k} \left(\frac{3N_A \rho}{4\pi M} \right)^{1/3} v_m, \quad (21)$$

where h is the Planck constant, k is the Boltzmann constant, N_A is the Avogadro constant, M is the atomic weight, and ρ is the density, and includes B , the bulk modulus as well G , the shear modulus, and

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{1}{v_p^3} \right) \right]^{-1/3}; \quad v_s = \sqrt{\frac{G}{\rho}}; \quad v_p = \sqrt{\frac{B+4G/3}{\rho}}. \quad (22)$$

Fig. 9 displays Debye temperature Θ (top) and melting temperature T_m (bottom) as functions of pressure for MH lattices, SC, BCC, and FCC. As well known, MH will climb to a very high Debye temperature, and could become a quantum liquid. Melting curves of metallic hydrogen as a function of pressure via the Lindemann melting law^{40,41}. Some samples: For SC lattice at $R = 3.1$, $\Theta = 57K$, and at $R = 1.12$ obtains $\Theta = 1779K$ at $P = 118$ Mbar. For BCC lattice at $R = 3.48$, $\Theta = 52K$, and at $R = 1.21$ obtains $\Theta = 1627K$ at $P = 147$ Mbar. For FCC lattice at $R = 3.88$, $\Theta = 41K$, whereas at $R = 1.21$ obtains $\Theta = 2114K$ at $P = 294$ Mbar.

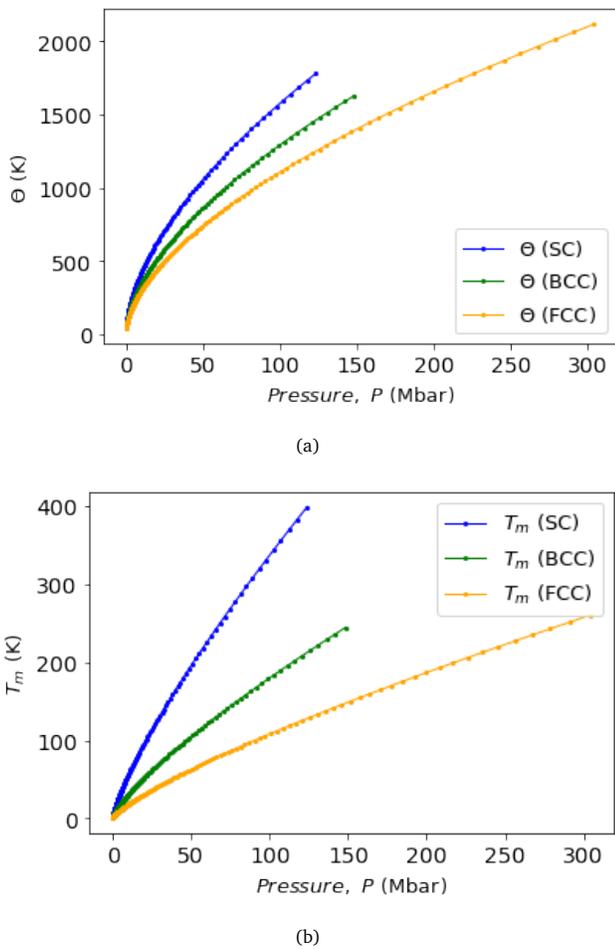


Fig. 9 We plot the Debye temperatures Θ (top panel) and melting points T_m (bottom panel) of MH in SC, BCC, and FCC lattice structure with the correlation with respect to the pressure, P .

Finally, as many authors predicted that metallic hydrogen is a superconductor below some critical temperature and others even argued that it might be a superconductor up to a room temperature^{42,43}. Following Koblischka, et al⁴⁴, we have used our MH energy curves via interpolation from Eq. (16) and formulate the transition temperature T_c for a MH superconductor:

$$T_c = \frac{h^2}{(2x)^2 2M_L n^{-2/3} \pi k}. \quad (23)$$

Here again h is the Planck constant; k is the Boltzmann constant; x is the atomic distance. A correction factor n is usually taken to be 1 for metals, and M_L is taken to be equal to the mass of a proton m_p .

In Fig. 10, we plot the possible values of transition temperature T_c calculated from Eq. (23) as a function of pressure for MH in SC, BCC, and FCC lattices, within a range where the energy is negative and pressure is positive. For the atomic distances, $x = R$ for SC; $x = (\sqrt{3}/2)R$ for BCC;

$x = R/\sqrt{2}$ for FCC. Samples: For SC lattice at $R = 3.1$, $T_c = 28K$ whereas for $R = 1.12$, $T_c = 215K$ and $P = 118$ Mbar. For BCC lattice at $R = 3.48$, $T_c = 30K$ whereas at $R = 1.21$, $T_c = 246K$, and $P = 147$ Mbar. For FCC lattice at $R = 3.88$, $T_c = 36K$ whereas for $R = 1.21$, $T_c = 369K$ and $P = 294$ Mbar.

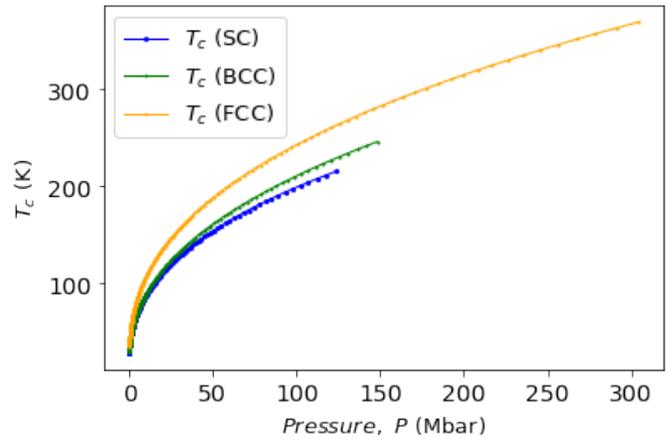


Fig. 10 We plot the transition temperature T_c as a function of pressure, P .

Although the experimental verification of superconductivity in MH is yet to be confirmed, but from the above theoretical calculations we see that the metallic hydrogen is a very good candidate for a high temperature superconductor.

7 Conclusion

The simplicity of the $D \rightarrow \infty$ limit causes the disappearance of derivatives from a Hamiltonian as well as $\hbar \rightarrow 0$, so is a true classical limit²⁷. It is different from a semiclassical approximation such as WKB theory for small \hbar . The simplicity of the $D = 1$ limit keeps derivatives in a Hamiltonian and is a true hyperquantum limit. Combining these extreme partner limits delivers the dimensional interpolation formula. It was tried out with two-electron atoms²⁰ and generalized out with few electron atoms and simple diatomic molecules²³. Here we find the interpolation approach is appropriate for metallic hydrogen. With beginning by Loeser²², we find the interpolation not only provided adequate energies but also the correct function forms of symmetry and lattice parameters. From the gradient and the curvature of the energy curves as a function of the lattice parameter R , we were able to calculate some important physical quantities. Among are the bulk and shear moduli, and three temperatures governed by pressure: the Debye temperature, the Lindemann melting temperature, and the critical transition temperature for superconductivity.

It is relatively easy to calculate the $D \rightarrow \infty$ and $D = 1$ limits, so the interpolation formula can predict results for

the physical dimension, $D = 3$. Therefore, D -scaling might approach the electronic structure of strongly correlated systems, where often traditional approaches are faced with computational difficulties!

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

S. K. would like to acknowledge funding by the U.S. Department of Energy (Office of Basic Energy Sciences) under Award No. DE-SC0019215.

References

- 1 E. Wigner and H. B. Huntington, *J. Chem. Phys.*, 1935, **3**, 764–770.
- 2 R. J. Hemley and H. K. Mao, *Phys. Rev. Lett.*, 1988, **61**, 857.
- 3 R. J. Hemley, M. Hanfland and H. K. Mao, *Nature*, 1991, **350**, 488–491.
- 4 R. J. Hemley, H. k. Mao, A. F. Goncharov, M. Hanfland and V. Struzhkin, *Phys. Rev. Lett.*, 1996, **76**, 1667.
- 5 M. Zaghoo, A. Salamat and I. F. Silvera, *Phys. Rev. B*, 2016, **93**, 155128.
- 6 I. F. Silvera and R. Dias, *Journal of Physics: Condensed Matter*, 2018, **30**, 254003.
- 7 P. Loubeyre, F. Occelli and P. Dumas, *Nature*, 2020, **577**, 631–635.
- 8 E. Babaev and N. W. Ashcroft, *nature physics*, 2007, **3**, 530–533.
- 9 E. Babaev, A. Sudbø and N. W. Ashcroft, *Nature*, 2004, **431**, 666–668.
- 10 E. Babaev, *Phys. Rev. Lett.*, 2002, **89**, 067001.
- 11 D. R. Herschbach, J. S. Avery and O. Goscinski, *Dimensional scaling in chemical physics*, Springer Science & Business Media, 2012.
- 12 D. Z. Goodson, M. López-Cabrera, D. R. Herschbach and J. D. Morgan III, *J. Chem. Phys.*, 1992, **97**, 8481–8496.
- 13 Z. Zhen and J. Loeser, in *Large-D Limit for N-Electron Atoms*, Springer, 1993, pp. 83–114.
- 14 S. Kais and D. R. Herschbach, *J. Chem. Phys.*, 1994, **100**, 4367–4376.
- 15 J. Rudnick and G. Gaspari, *Science*, 1987, **237**, 384–389.
- 16 J. G. Loeser, Z. Zhen, S. Kais and D. R. Herschbach, *J. Chem. Phys.*, 1991, **95**, 4525–4544.
- 17 S. Kais and D. R. Herschbach, *J. Chem. Phys.*, 1993, **98**, 3990–3998.
- 18 Q. Wei, S. Kais and D. Herschbach, *J. Chem. Phys.*, 2008, **129**, 214110.
- 19 Q. Wei, S. Kais and D. Herschbach, *J. Chem. Phys.*, 2007, **127**, 094301.
- 20 D. R. Herschbach, J. G. Loeser and W. L. Virgo, *J. Phys. Chem. A*, 2017, **121**, 6336–6340.
- 21 T. C. Germann and S. Kais, *J. Chem. Phys.*, 1993, **99**, 7739–7747.
- 22 J. G. Loeser, in *Large-D Limit for Metallic Hydrogen*, Springer, 1993, pp. 389–427.
- 23 K. J. B. Ghosh, S. Kais and D. R. Herschbach, *Frontiers in Physics*, 2020, **8**, 331.
- 24 D. D. Frantz and D. R. Herschbach, *Chemical physics*, 1988, **126**, 59–71.
- 25 A. L. Tan and J. G. Loeser, in *Simple molecules and variant scalings*, ed. D. R. Herschbach, J. Avery and O. Goscinski, Springer Netherlands, Dordrecht, 1993, pp. 230–255.
- 26 M. López-Cabrera, A. L. Tan and J. G. Loeser, *J. Phys. Chem.*, 1993, **97**, 2467–2478.
- 27 J. G. Loeser, J. H. Summerfield, A. L. Tan and Z. Zheng, *J. Chem. Phys.*, 1994, **100**, 5036–5053.
- 28 M. Born and R. D. Misra, *Mathematical Proceedings of the Cambridge Philosophical Society*, 1940, pp. 466–478.
- 29 I. R. Lapidus, *Am. J. Phys.*, 1975, **43**, 790–792.
- 30 I. R. Lapidus, *Am. J. Phys.*, 1982, **50**, 453–456.
- 31 B. I. Min, H. J. F. Jansen and A. J. Freeman, *Phys. Rev. B*, 1984, **30**, 5076–5083.
- 32 K. K. Mon, G. V. Chester and N. W. Ashcroft, *Phys. Rev. B*, 1980, **21**, 2641–2646.
- 33 P. Nozières and D. Pines, *Phys. Rev.*, 1958, **111**, 442–454.
- 34 E. E. Salpeter and H. S. Zapolsky, *Phys. Rev.*, 1967, **158**, 876–886.
- 35 P. M. Robitaille, *Progress in Physics*, 2011, **7**, 4005–.
- 36 S. A. Bonev, E. Schwegler, T. Ogitsu and G. Galli, *Nature*, 2004, **431**, 669–672.
- 37 K. K. Phani and D. Sanyal, *Materials Science and Engineering: A*, 2008, **490**, 305–312.
- 38 A. O. L., *Journal of Physics and Chemistry of Solids*, 1963, **24**, 909 – 917.
- 39 C. Li and Z. Wang, *Advances in Science and Technology of Mn+1AXn Phases*, Woodhead Publishing, 2012, pp. 197 – 222.
- 40 M. Ross and C. Shishkevish, *Molecular and metallic hydrogen*, Tech. Rep. (RAND CORP SANTA MONICA CA), 1977.
- 41 V. P. Trubitsyn, *Soviet Astronomy*, 1971, **15**, 303.
- 42 N. W. Ashcroft, *Phys. Rev. Lett.*, 1968, **21**, 1748–1749.

- 43 B. Cheng, G. Mazzola, C. J. Pickard and M. Ceriotti, *Nature*, 2020, **585**, 217–220.
- 44 M. R. Koblischka, S. Roth, A. Koblischka-Veneva, T. Karwoth, A. Wiederhold, X. L. Zeng, S. Fasoulas and M. Murakami, *Metals*, 2020, **10**, 158.