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Density Quantization of Metallic Hydrogen

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Abstract

A cellular model of atomic hydrogen is hypothesized in which the Fermi pressure due to a single foreign electron invading the cell is examined in lieu of the entire degenerate gas. The Schrödinger equation is then solved in a self-consistent fashion with Laplace's equation for the electronic cloud. The Wronskian of the two possible wave functions does not vanish because the homogeneous Neumann condition is applied to the surface of the cell, while the Coulomb singularity compels a solution to be generated from the origin. Two quantum numbers result, one for the energy and one for the density, thus there is a lower limit to the density at zero temperature. Further corrections for electron waves by the Born Von-Karmen conditions broadens the radial quantum number into a continuum, but with an absolute lower limit to the density given by the ground state solutions to the Schrödinger equation.

We obtain a bulk modulus of compressibility for metallic hydrogen of about $4{\cdot}66 \times 10^{12}$ dynes/g on the average over a pressure range of 1 to 25 megabars with a density range of 0·4 to 4 g/cc. This is about a factor of 2 greater than Wigner and Huntington's estimate (1935). The zero temperature pressure and density at a maximum is 20·05 Mb and 4·8 g/cc. At the density Wigner and Huntington propose (0·8 g/cc) for the metallic modification, we obtain a necessary pressure of 2·2 Mb. Wigner and Huntington suggest 0·25 Mb while Stewart's data (1956) suggest about 1 Mb. Recent investigations in the literature run the gamut from 1 to 20 Mb (Alder & Christian, 1960). Furthermore, we obtain a latent heat of fusion of 134·3 kcal/g at maximum density, which decreases to zero at 19·1 Mb. The result means that the metallic state of hydrogen exists only over a pressure range of 1 Mb and below 19 Mb, it is a viscoelastic fluid until the molecular solid, formed above 20 Mb begins to form a plasma.

1. *Introduction*

Experimental procedures in manufacturing metallic hydrogen are of two types—dynamic and static. Some megabars of pressure are believed to be necessary in order to achieve the product and this extreme requirement has been the cause of difficulty in its manufacture. Dynamic experiments are

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generally conducted with explosives, a procedure not only having laboratory disadvantages, but which yield results difficult to interpret. For, during the course of a dynamic test, the material may be carried away from its equilibrium state and therefore it is not clear if the actual derivative products of the lattice are being measured at the minimal point or not. Hence, it is not surprising that the explosive experiments of Alder and Christiansen gave a suspiciously large pressure of about 20 Mb for the formation of metallic hydrogen, while the calculations of Wigner and Huntington led to only 1 Mb. The static tests, which in principal are an improvement, carry with them the difficulty of containment because most materials enter a region of plastic flow at far below 0·5 Mb, generally one or two decades below. Hence a static test requires some clever engineering in the design of a high pressure vessel which will either remain rigid during the test or isochoric.

Since the original Wigner and Huntington work (1935), calculations have proceeded, principally by Hartree–Fock methods of their variation (Neece, Rogers & Hoover, 1971). The most recent one by Dynin (1972), based upon a sophisticated electron-phonon interaction, gives a value of 5·85 Mb for the transition pressure and this value is the next highest result to Alder and Christian (1960). Calculations by Ashcroft and Langreth (1967) apply a combination of perturbation theory and empirical formulae to the group of nearly free-electron metals. With a strong foothold on direct experimental evidence, they are able to calculate a number of mechanical properties quite accurately for these metals. With this confidence, Hubbard (1971) has used a method of Ashcroft (1967), based upon the polarization of ionic sites in an electronic plasma, in order to calculate the mechanical properties of metallic hydrogen. His results are in agreement with the Wigner and Huntington type essentially, which estimate a few megabars pressure for the transition pressure. Numerous calculations have been performed in the almost 40-year period since that original work was published, including the work by Kronig, DeBoer & Korringa (1946), who also corroborate these results. However, most of these calculations have been concerned with refinements of higher-order effects while adapting the basic approach of Wigner and Huntington for the kinetic and potential energies. Thus regardless of how fine the refinements, no principal deviation from the original calculation could really be expected, nor would one be anticipated were it not for such divergent properties found in high density matter by Bridgeman and Joffe as early as the last century. For example, in an isotropic state of stress, glass will withstand millions of p.s.i. pressure without fracture or plastic flow, and can even be made conducting in this way. Thus it is not clear that an extrapolation of successful results at ordinary pressure will be valid at ultra-high pressures because the material may enter some polymorphic state which cannot be reached by continuous extrapolation of the normal one.

All calculations commence with a statement of the Schrödinger equation for an electronic gas, they then proceed to replace the Laplacian by a kinetic energy of a degenerate Fermi sphere, while the electrostatic energy of some periodic configuration is added to produce a Hamiltonian. The result is an equation for a semi-classical plastic substance whose cohesive energy is given in the form of

$$E = -\frac{A}{r_s} + \frac{B}{r_s^2} + C \tag{1.1}$$

in which r_s is the Wigner–Seitz radius, a measure of the intracellular spacings. Then a minimum to equation (1.1) is found which yields both the radial spacing r_s and the cohesive energy E. This thermodynamic technique has met with remarkable success and so continues to be used. The ground state solutions to the Schrödinger equation are the zero temperature solutions, hence they should have no thermal fluctuation. Furthermore, a bound quantum mechanical system shows zero statistical fluctuation, so deviations in orbital size are impossible except for relativistic effects within the uncertainty principal. Thus it is not clear that derivative properties actually exist at zero temperature. Periodic electron waves over the entire lattice introduce a variable wave vector (k) which may then give the cohesive energy, derivative properties; however, these properties are external to the cell method. Within the logical consequences of that construction, both the energy and the density should be quantized, and this is consistent with the structure of the free hydrogen atom which has discrete energetic and radial quantum numbers. Therefore the cell should be related to the free atom by a continuity in this quantum number with a transition from discrete to continuous values as atoms are brought together from infinity at zero temperature. In this way it would avoid the designation of some intermediate point for this transition to take place; a point any theory would like to avoid no matter how attractive thermodynamic arguments are. Thirring (1956), in his classical text, uses thermodynamics to derive the structure of the hydrogen atom as a pedagogical exercise; however it is clear that this technique will not explain the Lamb shift. The success of semi-classical theories must simply be considered as concomitant explanations with ultimate theoretical limitations.

The formally correct procedure to this problem, we feel, is to solve the Schrödinger equation in a self-consistent way with Laplace's equation and obtain the quantum structure. Using statistical information from a Fermi–Dirac gas in Laplace's equation, as in the Thomas–Fermi method, denies the solution the complete eigenvalue character implicit in the structure of the Schrödinger equation. Nevertheless, the classical results are useful as guides and it appears that what saves solid hydrogen from instability is the collective degenerate effect of the Fermi electronic gas.

2. *The Hydrogen Atomic Cell*

The cell method, when normally applied to hydrogen, results in a number of formal difficulties which either reflect the limitations of the method or the correctness of the procedure which has been applied. Schrödinger, in seeking an explanation for the Balmer formula, was led to the equation of a hypergeometric function.

$$\left(\nabla^2 + \frac{2}{r} + E\right)\psi = 0 \tag{2.1}$$

By requiring the solution to be homogeneous at the near and far boundary, the eigenvalues were mapped onto a set of positive definite intergers (squared).

$$E = \frac{-1}{n^2} \tag{2.2}$$

The absence of $n = 0$ gave the atom stability while at the same time the hydrogen lines were dispersed in agreement with the Balmer formula. The condition that the solution squared be integrable over an infinite domain is equivalent to two homogeneous Dirichlet conditions –at the origin and infinity. Thus the Wronskian of the solution vanishes at the center of convergence about which the solutions are generated, and hence the solution is unique.

Kronig, DeBoer & Korringa (1946) have used equation (1.1) to explain the properties of a metallic hydrogen cell. In this case, the boundary condition becomes a homogeneous Neumann condition at the cell boundary.

$$\operatorname*{limit}_{r \to r_s} \frac{\partial \psi}{\partial r} = 0 \tag{2.3}$$

Then the eigenvalue spectrum is continuous and unstable,

$$E = -3/r_s \tag{2.3}$$

One would expect these eigenvalues to converge to those of the free atom as the cell size is increased to infinity, but clearly such a coalescence is impossible since the solutions represent two disjoint subsets of the class of hypergeometric function, one of which is the common Leguerre polynomial.

Of course, in the cell case, the collective Laplacian of the degenerate free electron gas is introduced to avoid the catastrophe of having the electron fall into the nucleus, but this implies that stability of the crystal is due to a plasma effect and it is difficult to associate the stability of an ordered phenomenon to an essentially disordered cause. It is consistent with the spirit of quantum mechanics to expect that every system which shows a discrete order on an atomic and molecular level should be quantized. Furthermore a discrete radial quantum number for a solid is also consistent with the structure of the isolated atom to which it is expected to evolve in a continuous fashion by a variation in the density.

Kronig, DeBoer & Korringa (1946) add the electronic Fermi energy of a degenerate free electron gas to their solution of Schrödinger's equation and obtain the equation of a deformable plastic substance which is now known as Jellium.

$$2{\cdot}21/r_s^2 - 3/r_s = 0 \tag{2.5}$$

To this, corrections of correlation and exchange energies can be added. The above equation has a thermodynamic minimum at $r_s = 1{\cdot}47$ giving a zero temperature cohesive energy very close to a Rydberg. Thus the heat of vaporization depends strongly on the correlation and exchange energies which are calculated by perturbation theory of other standard models.

The Wigner–Seitz analysis of a Bravais lattice yields an electrostatic energy of $1{\cdot}8004/r_s$ (Ryd.), to which the Fermi energy (in equation (2.4)) and other corrections may be added. Wigner and Huntington obtain a value of $r_s = 1{\cdot}5$ and $E = 1{\cdot}156$ Ryd. The increment above a Rydberg is the latent heat of vaporization which amounts to about 517°K for the diatomic gas—a rather significant figure for the planet Jupiter. Hydrogen molecules may also form crystals and an experimental pressure-energy plot for them has been given by Stewart (1956). Since the dissociation of the molecule is about one-third the energy of the atom, one can extrapolate his curves to this energy. The result indicates that molecular hydrogen could dissociate into the atomic crystal at about 1 Mb of pressure, providing there is no fluid phase intermediately. This result is an extrapolation to a value close to the ground state energy of the atomic form, therefore it is uncertain if the formation of the molecular crystal will help or hinder the formation of the atomic form.

The Schrödinger equation of a hydrogen cell in atomic units is

$$\left(\nabla^2 + \frac{2}{r} - V_{ee} + E\right)\psi = 0 \tag{2.6}$$

in which V_{ee} represents neighboring electronic interactions. We take this to be an external electron, either from the conduction band or a neighbor which undertakes invasion into the Wigner–Seitz cell. Because the foreign electron is indistinguishable from the cellular one, we require that Poisson's equation be satisfied as a concomitant condition. Thus we have two coupled equations.

Because of the Coulomb singularity, a solution must be generated from the origin. Since the homogeneous boundary condition applies to the far boundary, the Wronskian, in general, would not vanish at the point which the solutions are generated; thus there will be two independent solutions to this system of equations which can be combined into one complex form, $\Psi_1 + i\Psi_2$. Therefore the homogeneous Neumann condition (1955) then has two parts, both real and imaginary gradients must vanish at the far boundary. These two constraints will lead to discrete values for E and r_s—the radial quantum number.

Equation (2.6), the Schrödinger equation for a solid, contains the electron-electron potential which we take to be an external electron, either from the conduction band or a neighbor, which undertakes an invasion into the Wigner-Seitz sphere under consideration. Because this electron is indistinguishable from the cellular electron we require that Poisson's equation be satisfied in the following way:

$$\nabla^2 V_{ee} = \frac{-1{\cdot}5}{r_s^3}\,\psi^*\psi \tag{2.7}$$

as a concomitant condition. Thus we have a system of two equations, (2.6) and (2.7), in two unknowns, $V_{ee}(r)$ and $\psi(r)$.

Since solutions to Poisson's equation are analytic functions which reflect the complex arguments of its source, we shall obtain real functions for V_{ee}; hence the Hamiltonian will remain hermitian and the eigenvalues of the Schrödinger equation should then be real. However, the Hilbert space is a complex vector space so that a Neumann boundary condition has two parts. Both real and imaginary parts of the gradient must vanish. These two constraints then lead to discrete values for E, as well as r_s, a parameter in V_{ee}; hence, in principle, the crystal lattice should come out to a quantized structure as a result of V_{ee} as long as the wave function is complex. In the absence of foreknowledge, the solution of these two equations must proceed by successive iteration, and hence should start from the simplest assumption. We choose

$$\psi = 1 \tag{2.8}$$

as the simplest wave function which has the proper cellular boundary condition. Then the solution of equation (2.7) leads to

$$V_{ee} = \frac{r^2}{r_s^3} \tag{2.9}$$

a repulsive harmonic oscillator potential. We are further constrained by the static calculation of Wigner and Seitz (1934) who obtain $-1{\cdot}8004/r_s$ (Ryd.) for the average expectation value of V. Utilizing

$$-\tfrac{1}{2}V = \frac{1}{r} + \frac{1}{2}\frac{r^2}{r_s^3} \tag{2.10}$$

for the composite potential felt by an invading electron (in Rydberg units) one obtains

$$E = \frac{\int_0^{r_s} \psi^* V \psi r^2 d_r}{\int_0^{r_s} \psi^*\psi r^2 d_r} = \frac{-9}{5r_s} \tag{2.11}$$

a value which is within 2×10^{-7} percentile accuracy to the extensive calculation of Wigner and Seitz. The composite potential (2.10), when placed in the Schrödinger equation, should be expected to yield an evaluation of the kinetic energy in accurate association with the agreement to the static Wigner–Seitz calculation. Normally the Thomas–Fermi atomic model is used for this calculation (Salpeter, 1961). However, this model is also used for the isolated atom, hence it is not clear whether the difficulties mentioned between the two types of boundary conditions are surmounted or ignored.

Furthermore, one should expect that one more iteration would be possible by this method, perhaps by standard perturbation theory, if the accuracy of the dynamic solution is comparable to the static one just performed. It is clear that the series iteration for the potential must acquire an angular part with the r^4 term. This can be argued from the electrostatic images induced in a spherical electron cloud. In the body-centered cubic lattice, there would be eight such images. The angular distortion of the cell must be a vector which satisfies the symmetry requirement that the potential must be invariant to rotations in intervals of 90°.

$$\begin{aligned} \theta &\rightarrow \theta + n\pi/2 \\ \phi &\rightarrow \phi + n\pi/2 \end{aligned} \tag{2.12}$$

Since the potential must also be a basic solution to Poisson's equation, in which no additional change is generated by angular distortion, we must conclude that the predominating angular dependence of the potential must commence with the Legendre polynomial P_4. Hence we can write that

$$-V_{ee} = \frac{r^2}{r_s^3} + v_1 \frac{r^3}{r_s^4} + v_2 \frac{r^4}{r_s^5} Y_4^4(\theta, \phi) \tag{2.13}$$

in which v_1 and v_2 are constants normalized at each stage of iteration such that the total charge in the Wigner-Seitz sphere remains the same.

This implies that wave functions are not accurate beyond cubic order due to the angular distortion of the cell. We shall solve for the complete formal solution in first order but refrain from placing trust in any terms beyond the cubic ones.

In summary, this calculation is equivalent to separating the Schrödinger equation for two electrons into that for only one by subjecting the product wave function to a simple Hartree procedure. Since the electron-electron interaction is symmetric, it can be divided in half giving each equation an equal portion. The stable solution implies a long-range order which is periodic and thus confirms that the cell exists. The unstable solution does not necessarily imply a phase transition but that some plastic-fluid state describes the material, perhaps better described as visco-elastic.

3. *Formal Solution of Metallic Hydrogen Cells*

Given the Schrödinger equation for a foreign electron invading a spherical cell of hydrogen,

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{2}{r} + \frac{1}{r_s^3} r^2 - \frac{l(l+1)}{r^2} + E\right] \psi = 0 \tag{3.1}$$

in which r is in Bohr radii and the energy is in units of the ionization energy of the isolated hydrogen atom. We seek a series solution of the form

$$\psi = r^l \exp(ir^2/2r_s^{3/2}) \sum_{n=0}^{\infty} (\alpha_n + ir_s^{3/2}\beta_n) r^n \tag{3.2}$$

and are led to the coupled doublet recursion relation.

$$\alpha_{K+2} = -\frac{E\alpha_K + 2\alpha_{K+1}}{(K+2)(2l+K+3)} + \frac{2l+3+2K}{(K+2)(2l+K+3)}\beta_K \tag{3.3}$$

$$\beta_{K+2} = -\frac{E\beta_K + 2\beta_{K+1}}{(K+2)(2l+K+3)} - \frac{2l+3+2K}{(K+2)(2l+K+3)}\alpha_K/r_s^3 \tag{3.4}$$

which is asymmetrical only in the occurrence of the inverse cube dependence of r_s appearing in equation (3.4). If we were to set r_s equal to infinity and then set β_K equal to zero, we would obtain the solutions appropriate to the confluent hypergeometric series, in which case the Balmer formula would result from the inevitable choice to terminate the series before it becomes singular at infinity. On the other hand, the solutions for metallic hydrogen obtained by Kronig are displayed by cellular boundary conditions. In this case we find,

$$\psi \simeq r^l\left(1 - \frac{r}{l+1} + \frac{1}{2}\frac{Er^2}{2l+3} + \ldots \text{etc.}\right) \tag{3.5}$$

Then for $l = 0$, this wave function has an extremal at $r = r_s$, when

$$E = -3/r_s \tag{3.6}$$

the correct result of our antecedent (Kronig, DeBoer & Korringa, 1946).

We therefore appear to have incorporated and reconciled the results of Kronig and Winger-Seitz in our formulation of the Schrödinger equation so that no longer must a choice be made between the two developments. The coefficients may be computed as follows: First of all the principal term α_0 is a convenience which is factorable from all terms and may be set equal to unity in order to closely resemble our static choice in equation (2.8). This requires that the associated imaginary component be equal to zero $-\beta_0 = 0$. The next term removes the Coulomb parts of the series and we are led to

$$\alpha_1 = \frac{-1}{l+1}, \qquad \beta_1 = 0 \tag{3.7}$$

The remaining terms may now be generated automatically and, to fourth-order terms, are

$$\alpha_0 = 1; \qquad \beta_0 = \beta_1 = 0; \qquad \beta_2 = -1/(2r_s^3)$$

$$\alpha_1 = -\frac{1}{l+1} \qquad \beta_3 = \frac{1}{2(l+1)r_s^3}$$

$$\alpha_2 = \frac{1}{(l+1)(2l+3)} - \frac{E}{2(2l+3)} \qquad \beta_4 = \frac{E}{4(2l+3)r_s^3} + \frac{1}{2(l+1)(2l+3)r_s^3}$$

$$\alpha_3 = \frac{E(3l+4)}{6(l+1)(l+2)(2l+3)} - \frac{1}{3(l+1)(l+2)(2l+3)}$$

$$\alpha_4 = \frac{1}{6(l+1)(l+2)(2l+3)} - \frac{E}{12(l+1)(l+2)(2l+3)} \tag{3.8}$$

Terms of higher order than this see the appearance of r_s^6 in the denominator of the β's while cubic expressions addend the α coefficients. They are not particularly revealing and will be ignored with justification once their influence has been assessed.

If we now seek an extremal of the wave equation (equation (3.2)), we are led to two conditions by the independent obliteration of real and imaginary parts

$$\sum_{K=0}^{\infty} [(l+K)\alpha_K - B_{K+1}]r_s^K = 0 \tag{3.9}$$

$$\sum_{K=0}^{\infty} [\alpha_K + (l+K+2)B_{K+2}]r_s^K = 0 \tag{3.10}$$

in which we have defined $\beta = B/r_s^3$. These are two equations in two unknowns, E and r_s, for each integral value of l. Considering the propagation of higher than cubic terms in the denominator of β and corresponding effects upon the α coefficients will yield the following series within a series

$$\begin{aligned}\Bigg[(l+k)\alpha_K &+ \frac{(l+K-1)(2K+2l+5)(2K+2l+1)}{(K+1)(K+3)(2l+K+4)(2l+K+2)}\alpha_{K-1}\\ &+ \frac{(l+K+6)(2K+2l-1)(2K+2l+3)(2K+2l+7)(2K+2l+11)}{K(K+2)(K+4)(K+6)(2l+K+1)(2l+K+3)(2l+K+5)(2l+K+7)}\alpha_{K+1}\\ &+ \text{etc.} \ldots - B_{K+1}\Bigg] r_s^K = 0\end{aligned} \tag{3.11}$$

and

$$\begin{aligned}&\Bigg[\alpha_K+\frac{(2K+2l+3)(2K+2l+1)}{(K+1)(K+3)(2l+K+4)(2l+K+2)}\alpha_{K-1}\\&\frac{(2K+2l-1)(2K+2l+3)(2K+2l+7)(2K+2l+11)}{K(K+2)(K+4)(K+6)(2l+K+1)(2l+K+3)(2l+K+5)(2l+K+7)}\alpha_{K-2}\\&\qquad+\text{etc.}\ldots(l+K+2)B_{K+2}\Bigg]r_s^K=0+\text{etc.}\ldots\end{aligned}\tag{3.12}$$

in which a summation over the index K is implied, and all coefficients with negative index are zero.

In any algorithm for the computer, equations (3.3), (3.4), (3.9), and (3.10) should be used directly; however, we wish only to dissect these equations into some recognizable form. If we choose only the first and last terms in equations (3.11) and (3.12), which give us the lowest order solutions, then we obtain the following two results for the first three terms which contribute

$$E=-\frac{2(2l+3)}{(l+2)}\frac{1}{r_s}+\frac{2l(2l+3)}{(l+2)r_s^2}+\frac{2}{l+1}\tag{3.13}$$

and

$$r_s=\frac{l+1}{2}\left[1\pm\sqrt{(1-8l/(l+1))}\right]\tag{3.14}$$

because r_s must be real, we see that only the s wave solution exists, $l=0$, in which case we obtain two solutions for the radial quantum number, $r_s=0, 1$, which yield the corresponding energies of $E=-\infty, -1$. Both solutions of the free hydrogen atom and the catastrophic solid occur, i.e. one with a stable Bohr orbit at the Rydberg energy as well as the Kronig unstable solution. The energy agrees well with the Jellium model; however, the radial quantum number is off by 50%. Although this result has numerical limitations, it does show that to first order the solutions of Schrödinger, Wigner and Seitz, and Kronig find their reconciliation in a formalism such as this. We note that the Coulomb contribution at $l=0$ contains the Kronig catastrophic structure of $E=-3/r_s$; however, the kinetic energy adds a term of +2, hence the Rydberg energy occurs when the sphere is quantized to Bohr dimensions, $r_s=1$, in this order of approximation. Proceeding to increase the order of approximation to the principal terms of the energy as expressed in equations (3.10) and (3.11) we obtain a result which is, in some respects, more satisfying physically.

$$\begin{aligned}E=-\left(\frac{2(2l+3)}{(l+2)}+\frac{l}{3}\right)\frac{1}{r_s}+\frac{2l(2l+3)}{(l+2)r_s^2}+\frac{2}{l+1}\\+\frac{(2l+7)(2l+5)(2l+3)(l+1)}{5\,.\,3(l+3)(l+2)(l+2)}\end{aligned}\tag{3.15}$$

and

$$r_s = \frac{15}{4} \frac{(13l + 18)(l + 3)(l + 2)(l + 1)}{(2l + 3)[(2l + 7)(2l + 5)(2l + 1)(l + 1) + 30(l + 3)(l + 2)]} \tag{3.16}$$

Now the radial quantum number is real for all values of the angular momentum. For each value of l there is one unique value of r_s contrary to the Balmer formula in which r_s is any integer inferior to l. Numerically we obtain that

$$r_s(0) = 0{\cdot}628 \qquad \text{Bohr radii}$$

and

$$E(0) = -2{\cdot}194 \qquad \text{atomic units}$$

(the energy must be halved to obtain it per electron).

For the 's' state, $l = 0$. For the next level, $l = 1$, we obtain

$$r_s(1) = 0{\cdot}756 \qquad \text{Bohr radii}$$

$$E(1) = +3{\cdot}423 \qquad \text{atomic units}$$

The energy is quantized, but positive, and continues to be positive for all values of l above the ground state; hence the slightest non-zero contribution of the centrifugal potential yields a positive energy to a foreign electron which is imbedded in the Wigner–Seitz sphere.

Table 1 lists a few of these energies. We note that the Wigner–Seitz sphere increases for $l = 1$ above that of $l = 0$, then monatomically decreases. We also note that as the angular quantum number increases, the size of Wigner–Seitz cell decreases. This is because the energy becomes more and more positive, requiring greater and greater external pressure to hold the substance together and this pressure must keep the material compressed.

TABLE 1. Quantized metallic hydrogen (uncorrected)

l	r_s	E	$E/2$
0	0·627	−2·194	−1·097
1	0·756	+3·423	+1·712
2	0·678	+12·08	+6·04
3	0·581	+27·92	+13·96
4	0·499	+53·70	+26·85
5	0 435	+92·05	+46·03

4. *Electronic Lattice Dynamics*

The collective effects of the lattice are not fully accounted for in the cell model. This is especially true of the scale factors which contain the mass, i.e., what is known as the Rydberg constant and Bohr radius. The Born-von Karmen (1971) of the Bloch conditions may be used to calculate the effective mass of the electron in an actual periodic potential. We assume that the wave function can be expanded in a Fourier series,

$$\phi = \sum_K \exp(iK.r)r^l \exp(ir^2/2r_s^{3/2}) f_K(r) \tag{4.1}$$

in which K is a wave number which reflects the periodic size of the cell.

$$K = 2\pi in/r_s \tag{4.2}$$

Substituting the Fourier component (4.1) into the Schrödinger equation (3.1), gives the following:

$$\left[\nabla^2 + 2ik.\nabla - k^2\left(1 - \frac{m_0}{m_e}\right) + E - \frac{l(l+1)}{r^2} + \frac{2}{r} + \frac{r^2}{r_s^3}\right] r^l \exp(ir^2/2r_s^{3/2}) f_K = 0 \tag{4.3}$$

in which m_e is the effective mass of the invading electron, used to renormalize the Rydberg constant and the cell size, E is the cohesive energy calculated in the previous section. We take the vector k to be in the x-direction as a convenience. We then assume a solution in a square array of the form

$$f_K = \sum_{mn} (iK)^m x^m A_{mn} r^n \tag{4.4}$$

in which we can associate these coefficients with the original ones.

$$A_{0n} = \alpha_n + ir_s^3 \beta_n . \tag{4.5}$$

The coordinate system is non-orthogonal, and with this precaution the gradient and Laplace operations are carried out to yield,

$$\sum_{mn}\left[E - K^2\left(1 - \frac{m_0}{m_e}\right) + \frac{2l+3}{r_s^{3/2}} i + \frac{2}{r} + \frac{2l(m+n)}{r^2} + \frac{2i}{r_s^{3/2}}(m+n)\right.$$
$$\left. + 2iK\left(\frac{nx}{r^2} + \frac{m}{x}\right) + \frac{n(n+1+2m)}{r^2} + \frac{m(m-1)}{r^2}\right](iKx)^m r^n A_{mn} = 0 \tag{4.6}$$

By correspondence with relation (3.7) we rearrange this equation into the form

$$\left[\left(E + \frac{2l+3+2n}{r_s^{3/2}} i\right) + \frac{2}{r} + \frac{n(2l+n+1)}{r^2}\right] \mu^m A_{mn} r^{m+n} (iK)^m$$
$$+ \left[K^2(m_0/m_e - 1) + \frac{2m(l+n)}{r^2} + \frac{2im}{r_s^{3/2}} + \frac{2iK}{r} n\mu + \frac{2iKm}{\mu^2}\right.$$
$$\left. + \frac{m(m-1)}{\mu r^2}\right] \mu^m A_{mn} r^{m+n} (iK)^m = 0 \tag{4.7}$$

in which we have written

$$x = \mu r, \qquad \mu = \cos\theta \tag{4.8}$$

The first term in brackets is recognized as the original recursion relation, equations (3.3) and (3.4), which vanishes for all A_{0n}. Since we are justified in only going to quadratic order, we tabulate only the appropriate terms. Three of them are given by combinations of formulae (3.8), the other four are as follows:

$$\begin{aligned}
A_{10} &= \frac{1}{2}\left(\frac{m_0}{m_e} - 1\right)\\
A_{11} &= \left(1 - \frac{m_0}{m_e}\right)\Big/(l+1)\\
A_{12} &= \frac{1}{2}\left(1 - \frac{m_0}{m_e}\right)\left[\frac{1}{(l+1)(2l+3)} - \frac{E}{2(2l+3)}\right]\\
A_{20} &= \frac{-i}{k}\left\{\frac{1}{l+1} + \left(\frac{i}{2r_s^{3/2}} - \frac{3}{2}\right)\left(\frac{m_0}{m_e} - 1\right)\right\}
\end{aligned} \tag{4.9}$$

The wave function to this order is

$$\begin{aligned}
\phi_K = \exp(iK.r)r^l \exp(ir^2/2r_s^{3/2})\Bigg[1 - \frac{r}{l+1} + \bigg(\frac{1}{(l+1)(2l+3)} - \frac{E}{2(2l+3)}\\
- \frac{i/2}{r_s^{3/2}}\bigg)r^2 + \frac{iK}{2}\left(\frac{m_0}{m_e} - 1\right)\mu r + \frac{1}{(l+1)}\left(1 - \frac{m_0}{m_e}\right)iK\mu r^2\\
+ iK\left\{\frac{1}{l+1} + \left(\frac{m_0}{m_e} - 1\right)\left(\frac{i}{2r_s^{3/2}} - \frac{3}{2}\right)\right\}\mu^2 r^2 + \frac{iK\mu r^3}{2}\left(1 - \frac{m_0}{m_e}\right)\\
\times\left\{\frac{1}{(l+1)(2l+3)} - \frac{E}{2(2l+3)}\right\}\Bigg]
\end{aligned} \tag{4.10}$$

So far we have not used the normalization condition for the wave function. We normalize it to a unit cell. This is a real relation and guarantees us a real value for the effective mass. Expanded to quadratic order gives

$$\begin{aligned}
\phi_K^*\phi_K \simeq r^{2l}\Bigg[1 - \frac{2r}{l+1} - \frac{r^2}{(l+1)^2} + 2\left(\frac{1}{(l+1)(l+3)} - \frac{E}{2(2l+3)}\right)r^2\\
- \frac{K\mu^2 r^2}{r_s^{3/2}}\left(\frac{m_0}{m_e} - 1\right)\Bigg]\, r^2 + \frac{K^2}{4}\left(\frac{m_0}{m_e} - 1\right)^2 \mu^2 r^2\Bigg]
\end{aligned} \tag{4.11}$$

We now apply the condition

$$\int_{-1}^{+1} d\mu \int_{0}^{r_s} \phi_K^* \phi_K r^2 \, dr = \frac{3{r_s}^3}{8\pi} \tag{4.12}$$

and obtain the requirement

$$\frac{1}{2l+3} - \frac{r_s}{(l+1)(2l+1)} - \frac{{r_s}^2}{(l+1)^2(2l+5)} + 2\left(\frac{1}{(l+1)(l+3)} - \frac{E}{2(2l+3)}\right)$$

$$\times \frac{{r_s}^2}{2l+5} - \frac{2K^2(m_e/m_0 - 1)}{3r_s^{3/2}(2l+5)}{r_s}^2 + \frac{K^2}{6}\frac{(m_e/m_0 - 1)^2}{2l+5}{r_s}^2 = \frac{8\pi r_s}{3} \tag{4.13}$$

The dominant term gives

$$m_e = m_0/(1 + 2\pi r_s^{3 \cdot 5}/K^2) \tag{4.14}$$

in which $K = 2\pi n/r_s \geqslant 10$ for the ground state and n is a positive definite integer. The effective mass of the ground state is then $m_e = m_0/0{\cdot}981$. According to Kronig, who used a method due to Bardeen (1938), the effective mass of the uninvaded cell is altered by a factor of 0·966 (Schweker, 1962). Thus the first-order calculation agrees well with the Bardeen value. Bardeen obtains his number by evaluating the kinetic energy by means of a solution to the Schrödinger equation. Since we have carried out our solution a few steps further, we should be able to obtain a correction to his term. Equation (4.13) is a quadratic equation and can be solved, in which case we obtain a value of 0·772 rather than 0·981. This then alters the size of the crystal as well as the zero temperature cohesive energy.

Normally one must correct the static energy for the exclusion principle. This is the zero point kinetic energy of electrons which is taken as the average Fermi energy. However, this term is accommodated by the Laplacian since we actually solved the Schrödinger equation. Three classical corrections are in order, the first being Dirac's exchange term which accounts for electrons of parallel spin repelling one another, more so than anti-parallel spin. This is an attractive term since it results from the cross terms of the antisymmetrized wave function whose value may be found in Schweber (1962). It amounts to

$$E_x = -\frac{0{\cdot}458}{r_s} \tag{4.15}$$

A further correction to this term by Gell-Mann and Brueckner (1957) accounts for the omission of ionic fields except for a homogeneous average effect. Hence to second order, equation (4.15) must be supplemented by the correlation energy

$$E_c = -0{\cdot}062 \, ln r_s - 0{\cdot}096 \tag{4.16}$$

These are the principal terms of a power series, hence valid for $r_s < 1$. Both these corrections tend to bind the lattice tighter; however, one additional term is repulsive and this is the change in ionic potential and kinetic energy due to ionic vibrations. The use of a sophisticated phonon spectrum would hardly be consistent with the previous corrections so that we follow the procedure of Salpeter and use the quantum theory of small oscillations for small nuclear displacements from the lattice site. This gives the contribution of zero point energy,

$$E_z = 3\sqrt{(m/M)}/r_s^{1{\cdot}5} \tag{4.17}$$

which is small due to the appearance of the electron-hydrogen mass ratio (square root).

The sum of these corrections is as follows:

$$\Delta E = -\frac{0{\cdot}458}{r_s} - 0{\cdot}062 \ln r_s - 0{\cdot}096 + 0{\cdot}07/r_s^{1{\cdot}5} \tag{4.18}$$

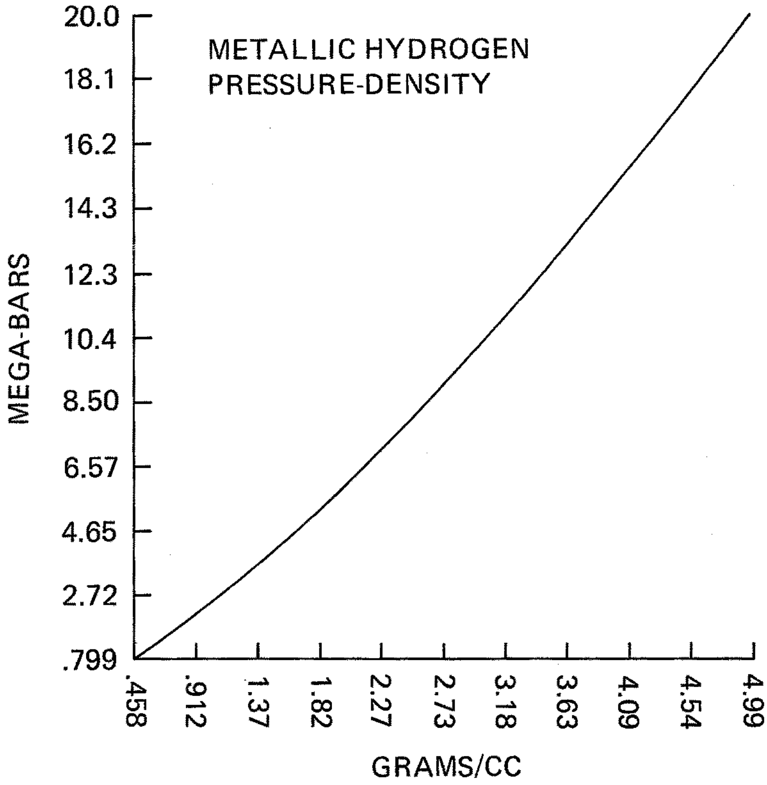

Figure 1.

For a body centered cubic lattice we have the following relation between the length of the cube edge (a) and the nearest neighbor distance (d)

$$n_e = \tfrac{1}{2}a^3 = 4d^3/(3\sqrt{3}) \tag{4.19}$$

Therefore the volume of a cube is

$$V = 8\pi r_s^3/3 \tag{4.20}$$

The sum total of these corrections produces a zero temperature cohesive energy of $-1{\cdot}142$ Rydbergs, a cell radius of 0·8137 Bohr radii, a density of 4·8 g/cc, a pressure of 20·05 Mb and a latent heat of 134·4 kcal/g. The pressure over other ranges of density represents variations in the wave vector K of equation (3.16) and hence the differentiation of the energy from the upper and is justified to obtain the pressures below the above values. This leads to the following expression.

$$P = 5{\cdot}85\,\frac{m_e}{m_0}\left[\left(\frac{2l+3}{l+2} + \frac{l}{6} + 0{\cdot}458\right)\bigg/ r_s^4 - \frac{2l(2l+3)}{l+3}\,\frac{1}{r_s^5} - \frac{0{\cdot}062}{r_s^3} + \frac{0{\cdot}0356}{r_s^{4\cdot 5}}\right] \tag{4.21}$$

in which m_e/m_0 is the effective mass ratio.

A plot of this curve as a function of density is given in Fig. 1. The curve appears to be rather linear with minimum at a density well into the molecular range. Therefore there is no zero pressure form for metallic hydrogen. Figure 1 passes close to the classical results in the theoretical literature at lower pressure; however, within the sphere of consideration of this theory, this lower pressure range is fluid and the metallic region has a range too short to be of practical significance to the equation of state. It is of importance only in that the heat of fusion changes sign with an increase in density with a large heat capacity equivalent to the temperature change of 2300°K. This is an ample heat sink to thermal content of the planets.

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