

Comparison of theoretical models for metallic hydrogen*

M. Ross and A. K. McMahan

Lawrence Livermore Laboratory, University of California, Livermore, California 94550

(Received 29 September 1975)

Calculations of the Gibbs free energy of metallic hydrogen were made by the four most common methods and shown to be in good agreement with each other. In addition it is shown that the free-electron correlation energy commonly used in calculations on metallic hydrogen is approximately four times larger than the spread over the Gibbs free energy as calculated by the four methods. Because the free-electron correlation energy expression may be in error by a factor of 2 or 3, it represents the largest source of uncertainty currently facing an *ab initio* treatment of the metallic hydrogen phase.

A crucial feature of the equation of state of hydrogen in the 1–20-Mbar range is the correct positioning of the molecular-to-metallic phase transition, which is expected to involve a 25% volume change.¹ While a proper calculation of the phase transition requires accurate equations of state for both molecular and metal phases, we have restricted this study to the calculation of the properties (energy, pressure, and Gibbs free energy) of the metal phase.

There are four methods by which the equation of state of hydrogen (and other metals) are commonly computed: electron-band methods such as the augmented plane wave (APW); free-electron perturbation theory to third order (PERT); the linear combination of atomic orbitals (LCAO); and the Wigner-Seitz (WS) method.² At the outset we may ask ourselves, "which is the best method for calculating the equation of state" and "how much difference does it make which method is used?" Inasmuch as none of the theoretical methods is exact, and each method is an approximation, a certain amount of subjectivity automatically enters into a discussion of the first question. However, we can answer the second question quantitatively (despite the fact that no experimental data exist) by comparing calculations for all four methods. This paper presents such a numerical comparison for the case of fcc metallic hydrogen. The numbers presented come from the published literature as well as from our own calculations using the first three methods.

To summarize, we found that the pressure differences between the highest and lowest values, as computed by the four methods, differed by an average of 0.35 Mbar between 0 and 10 Mbar. (We believe that this represents good agreement between methods.) The average spread in Gibbs free energy over this pressure range is 0.03 Ry; however, the free-energy contribution resulting from the inclusion of electronic correlation energy amounts to 0.13 Ry, or over four times the un-

certainty between the methods.

The calculations of energy, pressure, and Gibbs free energy by the four methods cited above are listed in Tables I–III under their corresponding headings. To simplify the problem of comparing the four methods, we felt the comparison should be made at the level of the Hartree-Fock Hamiltonian (i.e., we neglected correlation effects). Thus, the figures tabulated in columns 2–5 do not include contributions from electron correlation (or from zero point motion). Column 6 in each table (labeled, respectively, $\Delta E, \Delta P, \Delta G$) is the total spread of the calculated property over the four models considered. It is the difference between the highest and lowest values in columns 2–5. Column 7 is an estimate of the zero-point contributions by the expression for the zero-point energy

$$E_z = 0.0675v^{-1/2} \text{ Ry}, \quad (1)$$

where v is the atomic volume in a.u. This expression, cited by Trubitsyn,³ is based on the work of Kopyshv.⁴ Results obtained with this model are in very good agreement with the metallic hydrogen Debye temperatures calculated by Neece *et al.*,⁵ who used the well-known electrostatic model of Fuchs. In spite of possible inaccuracies, the model suffices to approximate the magnitude of the zero-point properties. The contributions resulting from electron correlation (column 8) are based on the free-electron gas formula

$$E_{\text{corr}} = -0.1303 + 0.0495 \ln r_s, \quad (2)$$

where $\frac{4}{3}\pi r_s^3 = 1/\rho$, ρ is the electron density, and r_s is an electron sphere radius. This expression, used by Neece *et al.*, is an analytic fit at 0 K to the detailed numerical work of Graboske and De Witt,⁶ who evaluated the generalized ring term for arbitrary density and temperature. Near zero temperature and high density, the quantum-mechanical ring term is the leading term after the first-order exchange term, and thus is the major

TABLE I. Model comparisons (energy is in Ry).

V (cm ³ /mol H)	APW	PERT (3rd order)	LCAO	WS	ΔE	E_z	E_{corr}
1.855	-0.968	-0.943 -(0.029) ^a	-0.932 -(0.950) ^b	-0.970	-0.038	0.015	-0.104
1.0	-0.926	-0.915 -(0.024)	-0.901 -(0.902)	-0.933	-0.031	0.020	-0.114
0.9	-0.910	-0.901 -(0.0235)	-0.886	-0.918	-0.032	0.021	-0.116
0.8	-0.887	-0.881 -(0.023)	-0.865	-0.898	-0.033	0.023	-0.118
0.7	-0.856	-0.852 -(0.022)	-0.836	-0.867	-0.031	0.024	-0.120
0.6	-0.810	-0.809 -(0.021)	-0.793	-0.823	-0.030	0.026	-0.123
0.5	-0.742	-0.745 -(0.020)	-0.729	-0.758	-0.029	0.029	-0.126

^a Third-order contribution.^b Reference 11.

contribution to the correlation energy of the free-electron gas. This expression differs by less than 10% from the more common Nozières-Pines⁷ interpolation formula

$$E_{\text{corr}} = -0.115 + 0.031 \ln r_s.$$

Turning now to the four methods mentioned earlier, we first calculated the properties of metallic hydrogen using the self-consistent APW method, with the $X\alpha$ exchange approximation, where α is equal to $\frac{2}{3}$. As noted earlier, correlation effects were excluded from the results (columns 2–5). Another set of self-consistent APW calculations (not shown in the tables) was made using Eq. (2) as a local correlation energy expression in which $\rho = \rho(r)$. In this approximation

the total correlation energy is written

$$\int \epsilon_{\text{corr}}(r) \rho(r) d\mathbf{r}, \quad (3)$$

where $\epsilon(r) = -0.1303 + 0.0495 \ln r_s$ [as in Eq. (2)], $\frac{4}{3}\pi r_s^3 = 1/\rho(r)$, and $\rho(r)$ is the local charge density in the APW calculation. The variational principle is then applied to solving the eigenvalue problem. The computed properties differed by no more than 1%, the same as if the free-electron correlation had been added directly to the “uncorrelated” APW calculations by using the free-electron expression [Eq. (2)], with $\rho = 1/v$.

The results for the Wigner-Seitz method, also done self-consistently, were taken from the work of Neece *et al.* They used $\alpha = \frac{2}{3}$ in their calcula-

TABLE II. Model comparisons (pressure is in Mbar).

V (cm ³ /mol H)	APW	PERT (3rd order)	LCAO	WS	ΔP	P_z	P_{corr}
1.855	+0.067	-0.115 (0.059) ^a	-0.068	+0.112	0.23	0.05	-0.12
1.0	1.85	1.58 (0.094)	1.63	1.71	0.27	0.13	-0.22
0.9	2.52	2.22 (0.10)	2.27	2.35	0.30	0.16	-0.24
0.8	3.49	3.16 (0.11)	3.21	3.28	0.33	0.19	-0.27
0.7	4.93	4.56 (0.12)	4.61	4.65	0.37	0.23	-0.31
0.6	7.20	6.76 (0.14)	6.81	6.89	0.44	0.29	-0.36
0.5	11.02	10.49 (0.16)	10.54	10.56	0.53	0.38	-0.43

^a Third-order contribution.

TABLE III. Model comparisons (Gibbs free energy is in Ry).

V (cm ³ /mol H)	APW	PERT (3rd order)	LCAO	WS	ΔG	G_z	G_{corr}
1.855	-0.958	-0.959 -(0.021) ^a	-0.942	-0.953	0.017	0.022	-0.120
1.0	-0.785	-0.795 -(0.017)	-0.777	-0.803	0.026	0.030	-0.131
0.9	-0.737	-0.748 -(0.017)	-0.730	-0.757	0.027	0.032	-0.132
0.8	-0.675	-0.689 -(0.016)	-0.670	-0.698	0.028	0.034	-0.134
0.7	-0.593	-0.609 -(0.015)	-0.595	-0.619	0.026	0.036	-0.137
0.6	-0.481	-0.499 -(0.0146)	-0.482	-0.508	0.027	0.039	-0.139
0.5	-0.322	-0.356 -(0.014)	-0.327	-0.356	0.034	0.043	-0.142

^a Third-order correction.

tions and also included correlation energy. The correlation energy was subtracted out of their calculations by using Eq. (2), with a constant ρ . In so doing, we were guided by the insight acquired from the "correlated" APW calculations. These calculations, with the correlation energy subtracted out, are shown in the tables.

The calculations for the free-electron perturbation theory also omit the electron correlation and were done to third order using Hammerberg and Ashcroft's method.⁸ They discuss perturbation theory in some detail and show numerically that the sum of the fourth-order terms in hydrogen are negligible. The third-order terms shown in the lower parentheses are not negligible although they have been omitted by most of the previous workers who used this model to compute the metallic hydrogen phase transition.

The LCAO calculations were done with a computer program coded at LLL, but they were based on a method first proposed by Abrikosov⁹ and more recently employed by Harris and co-workers.¹⁰ As first suggested by Abrikosov, the Bloch wave function for the k th electron is written

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_n \phi(\mathbf{r} - \mathbf{R}_n), \quad (4)$$

where the sum is over all atoms in neighboring lattice sites located at R_n , $\phi(r)$ is a single Slater-type orbital of the form $e^{-\alpha r}$, and α is varied to minimize the energy and satisfy the variational principle. Note that the LCAO, WS, and APW calculations are all self-consistent. The wave function of Eq. (4) was used in all the calculations shown in the LCAO column. This is an exact minimal-basis-set Hartree-Fock calculation. It treats the exchange energy exactly and does not

employ a local free-electron approximation as did the previous three models. However, inspection of the results does show that the computed exchange is very close to that which would be computed by a free-electron local exchange potential in which $\alpha = \frac{2}{3}$. The terms in parentheses in the LCAO column in Table I are from (or interpolated from) the work of Ramaker *et al.*,¹¹ who included a sum over reciprocal-lattice vectors in their wave function.

Ramaker *et al.* wrote their wave function as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\vec{\mathbf{K}}} C(\vec{\mathbf{K}}, \vec{\mathbf{K}}) e^{i(\vec{\mathbf{k}} + \vec{\mathbf{K}})\cdot\mathbf{r}} \sum_{n=1} \phi(\mathbf{r} - \vec{\mathbf{R}}_n), \quad (5)$$

where k is restricted to the first Brillouin zone, $\vec{\mathbf{K}}$ is a reciprocal-lattice vector, and $\phi(r)$ is a single Slater-type orbital. The coefficients $C(\vec{\mathbf{k}}, \vec{\mathbf{K}})$ are determined as functions of $\vec{\mathbf{K}}$. Elimination of the sum over $\vec{\mathbf{K}}$ reduces (5) to (4). Tables I and II show that above 1 Mbar the inclusion of the sum over $\vec{\mathbf{K}}$ leads to no further lowering of the energy. Unfortunately, Ramaker did not compute metallic pressures. Correlation energy cannot presently be included in the LCAO method in any tractable fashion consistent with this method.

The results in the tables show clearly that the correlation contributions to the energy and Gibbs free energy are about four times larger than differences in total energy between the four models. They are of the same order as the differences in the case of pressure. Thus, the accuracy of this approximation will have considerable effect on the calculation of the metallic transition. Local free-electron correlation, potential-energy expressions [such as Eq. (3)] have been used in atomic calculations in the same spirit as local free-electron exchange; however, the results

have not been as good. The correlation energy appears to be a much more sensitive function of the total wave function than is exchange energy. Tong and Sham¹² used the free-electron prescription and their computed correlation energies were twice as large as those estimated by Clementi¹³ from experimental energies. Similar results have been obtained by Kim and Gordon¹⁴ who found that the free-electron expression overestimated the correlation energy by a factor of 3 in small molecules (such as He, Li, and Li⁺) and by a factor of 2 for argon. Monkhorst and Oddershede¹⁵ have used the random-phase approximation to calculate the correlation energy in metallic hydrogen using the Hartree-Fock Bloch functions of Harris and co-workers. They arrived at a correlation energy approximately three-fourths as large as that calculated from free-electron theory.

To illustrate the effect of the uncertainty in correlation energy on the molecular-to-metallic transition pressure, we have made use of the molecular-phase results of Etters *et al.*¹⁶ (obtained with the spherically averaged potential). Taking the APW result for the metal, including the full free-electron correlation and zero-point energies, we calculate a transition pressure of 1.9 Mbar. Inclusion of only half of the correlation energy leads to an increase in the predicted pressure to 3.5 Mbar. Calculations made with other

molecular-phase equations of state¹ lead to similar results. These findings allow us to conclude that if the free-electron expression does overestimate the correlation energy by a factor of 2, then previous estimates of the transition pressure will be nearly a factor of 2 too small. These estimates do not include the uncertainties in the molecular-phase equation of state, which at the present time are at least as great.

For the sake of completeness, a comment should be made on the structural dependence of the energy. The energy differences found by Brovman *et al.*¹⁷ in their PERT calculations for various lattice types, in particular the 0.018-Ry difference between the most stable anisotropic structure and the least stable cubic structure, is not only considerably smaller than the correlation energy, but also less than the spread between the four models considered here.

In summary, free-electron formulas for the correlation energy are approximately four times larger than the spread in total Gibbs free energies of the four most common models, and are also considerably larger than structural energy differences. Because expressions commonly used for this term may be in error by a factor of 2 or 3, it represents the largest source of uncertainty facing current *ab initio* treatments of the metallic phase of hydrogen.

*Work performed under the auspices of the U. S. Energy Research and Development Administration, under contract No. W-7405-Eng-48.

¹M. Ross, *J. Chem. Phys.* **60**, 3634 (1974).

²J. M. Ziman, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz and D. Turnbull (Academic, New York, 1971), Vol. 26, p. 1.

³V. P. Trubitsyn, *Fiz. Tverd. Tela* **8**, 862 (1966) [*Sov. Phys.-Solid State* **8**, 688 (1966)].

⁴B. P. Kopyshchev, *Dokl. Akad. Nauk SSSR* **161**, 1067 (1965) [*Sov. Phys.-Dokl.* **10**, 338 (1965)].

⁵G. A. Neece, F. J. Rogers, and W. J. Hoover, *J. Comput. Phys.* **7**, 621 (1971).

⁶H. Graboske, Jr., and H. de Witt (unpublished).

⁷P. Nozières and D. Pines, *Nuovo Cimento* **9**, 470 (1958).

⁸J. Hammerberg and N. W. Ashcroft, *Phys. Rev. B* **9**, 409 (1974).

⁹A. A. Abrikosov, *Astron. Zh.* **31**, 112 (1954).

¹⁰F. E. Harris and H. J. Monkhorst, *Phys. Rev. Lett.* **23**, 1026 (1969); and in *Computational Methods in Band Theory*, edited by P. W. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971), p. 517.

¹¹D. E. Ramaker, L. Kumar, and F. E. Harris, *Phys. Rev. Lett.* **34**, 812 (1975).

¹²B. K. Tong and L. J. Sham, *Phys. Rev. A* **1**, 139 (1965).

¹³E. Clementi, *J. Chem. Phys.* **38**, 2248 (1963); **39**, 175 (1963); **42**, 2783 (1965).

¹⁴Y. S. Kim and R. G. Gordon, *J. Chem. Phys.* **60**, 1842 (1974).

¹⁵H. J. Monkhorst and J. Oddershede, *Phys. Rev. Lett.* **30**, 797 (1973).

¹⁶R. D. Etters, R. Danilowicz, and W. England, *Phys. Rev. A* **12**, 2199 (1975).

¹⁷E. G. Brovman, Y. Kagan, and A. Kholas, *Zh. Eksp. Teor. Fiz.* **61**, 2429 (1971) [*Sov. Phys.-JETP* **34**, 1300 (1972)].