

# ELECTRIC FIELD DISTRIBUTION OF THE PALLADIUM CRYSTAL LATTICE

K. J. Bunch and R. W. Grow

Cold Fusion Institute  
University of Utah  
Salt Lake City, Utah 84112

## ABSTRACT

Palladium has always been a metal of interest for its hydrogen absorption qualities [1] and, more recently, for its use in cold fusion experiments [2]. An atomic model of the metallic crystal would give a better overall understanding of the palladium-hydrogen system. Unfortunately, a computer simulation of the wave mechanical properties of palladium based on solving the three-dimensional Schrödinger equation is a major undertaking [3, 4] that is probably unnecessary for calculating many useful characteristics of palladium. A simpler approach, based on a Thomas-Fermi model [5] for palladium, is proposed by the authors. This semiclassical model averages the effects of all the electrons within an atom to approximate the electric field distribution everywhere. Overlapping these distributions approximates the electric fields within the palladium crystal. This model predicts a crystal that is a bit too stiff, but overall it gives reasonable results; it is also simple to use. It is expected that this model will broaden the understanding of the interaction of hydrogen with palladium.

## INTRODUCTION

This paper presents preliminary investigations into the electric field distribution within palladium metal based on the Thomas-Fermi statistical model [5-7]. This model has a long and fruitful history [8-12], but it has largely been displaced by self-consistent field techniques [3, 13-20] for calculating molecular properties. Recently, however, Lieb and Simon [10] have revived interest in the Thomas-Fermi model by showing that the model becomes exact as the atomic number approaches infinity. Further, various corrections have been proposed to make this model more exact for finite atomic number [21-24].

## THE THOMAS-FERMI MODEL

The basic Thomas-Fermi model [7] assumes the electrons in a central field satisfy Fermi-Dirac statistics and that the potential varies little within an electron wavelength. The number of electron states contained within a cube of length  $L$  is given by

$$N = 2 \left( \frac{L}{2\pi} \right)^3 dk_x dk_y dk_z \quad (1)$$

The factor of 2 comes from the 2 possible electron spin states. The number of states for which the momentum  $p = \hbar k$  is less than  $P_0$  is

$$2 \left( \frac{L}{2\pi} \right)^3 \int_0^{P_0/\hbar} \int_0^\pi \int_0^{2\pi} k^2 dk \sin \theta d\theta d\phi = \frac{P_0^3 L^3}{3\pi^2 \hbar^3} \quad (2)$$

Assuming a central field, the maximum kinetic energy an electron can have is  $-V(r)$ ; otherwise, electrons would escape the field. A relation between the density of electrons and the potential energy is then

$$n(r) = \frac{[-2m V(r)]^{3/2}}{3\pi^2 \hbar^3} \quad (3)$$

From Poisson's equation,

$$\nabla^2 V(r) = \frac{-n(r)}{\epsilon} \quad (4)$$

A differential equation for the potential is obtained by eliminating the electron density:

$$\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d(-V)}{dr} \right] = \frac{[-2m V(r)]^{3/2}}{3\pi^2 \epsilon \hbar^3} \quad (5)$$

Making the following substitutions:

$$V(r) = \frac{-Ze^2}{4\pi\epsilon r} \phi = \frac{-14.3998}{r} \phi$$

(r in Å, V in e.v.) (6)

$$r = bx \quad (7)$$

$$b = \frac{0.885341 a_0}{Z^{1/3}} = \frac{0.468502}{Z^{1/3}} \quad (8)$$

where Z is the nuclear charge and  $a_0$  is the Bohr radius (0.5292 Å). Equation 5 becomes

$$\frac{d^2 \phi}{dx^2} = \frac{\phi^{3/2}}{\sqrt{x}} \quad (9)$$

which is the Thomas-Fermi equation. A numerical solution was found by Bush and Caldwell [25] sufficiently accurately for the purposes of this paper. For palladium, Z = 46 and

$$V(r) = \frac{-662.39}{r} \phi \quad (10)$$

$$r = 0.13076x \quad (11)$$

For the ionization energy of a palladium atom stripped of 1 electron,  $\phi$  has to drop from its value at  $x = 0$  ( $\phi = 1$ ) to  $1/Z = 0.0217$ . From the tabulated values of  $\phi$  given by Bush and Caldwell [25],

$$x = 10.16$$

$$r = 1.33 \text{ Å}$$

$$V(r) = 10.8 \text{ e.v.}$$

The actual ionization energy is 8.3 e.v. [26], reasonably close to that predicted by the Thomas-Fermi model. As a further example, for a palladium atom stripped of 4 electrons, the measured radius is 0.64 Å [26].  $\phi = 4/46 = 0.087$  and

$$x = 4.7$$

$$r = 0.615 \text{ Å}$$

$$V = 93.7 \text{ e.v.}$$

The results are reasonable.

## THE PALLADIUM LATTICE MODEL

The palladium lattice is assumed to be a simple superposition of Thomas-Fermi atoms. The electric potential at any point in space is assumed to be the superposition of the potentials from all the neighboring atoms. The atoms themselves are assumed to be noninteracting, and so this model cannot predict the binding energy of the palladium metal. Even if the interaction is taken into account, however, the Thomas-Fermi model is unable to produce a binding interaction [27, 28]; corrections to this model can produce binding, however [12].

Palladium is a face-centered cubic structure, and if a single atom is placed at the center of an x, y, z coordinate system, any other atomic center can be located through the primitive vectors [4]

$$\vec{t}_1 = \frac{r}{\sqrt{2}} (\hat{y} + \hat{z}) \quad (12)$$

$$\vec{t}_2 = \frac{r}{\sqrt{2}} (\hat{x} + \hat{z}) \quad (13)$$

$$\vec{t}_3 = \frac{r}{\sqrt{2}} (\hat{x} + \hat{y}) \quad (14)$$

$$\vec{R} = \ell \vec{t}_1 + m \vec{t}_2 + n \vec{t}_3 \quad (15)$$

r is the nearest neighbor distance (2.49 Å [29]) and  $\ell, m, n$  are the integer indices 0,  $\pm 1, \pm 2, \dots$ . At any location x, y, z in the lattice, the distance to any atomic center is given by

$$P = \frac{r}{\sqrt{2}} \left[ (m + n - x)^2 + (\ell + n - y)^2 + (\ell + m - z)^2 \right]^{1/2} \quad (16)$$

The calculation of the potential anywhere within the lattice involves solving the Thomas-Fermi differential equation (Eq. 9), and summing up the contributions to the potential at each of the distances given by Eq. 16. The indices are increased until the contributions to the potential from higher indices is negligible.

### PREDICTED BULK MODULUS AND VELOCITY OF SOUND

The bulk modulus is a measure of the compressibility of a material and the stiffness of the crystal lattice. It is defined by [26]

$$B = \frac{-\Delta P}{\Delta V/V} = -V \frac{dP}{dV} \quad (17)$$

where  $P$  is the pressure on all sides of the material, and  $V$  is the volume given by [26]

$$V = \gamma r^3 \quad (18)$$

where  $r$  is the nearest neighbor distance and  $\gamma = 2^{-1/2}$  for the face-centered cubic structure. The pressure in Eq. 17 is the change of energy of the crystal with respect to a change in volume

$$P = - \frac{dU}{dV} \quad (19)$$

so that the bulk modulus becomes

$$B = \frac{1}{9\gamma r} \left[ \frac{-2}{r} \frac{dU}{dr} + \frac{d^2U}{dr^2} \right] \quad (20)$$

Consider removing the atom at the origin of the coordinate system and replacing it with a test charge. The bulk modulus can be determined by calculating the potential changes at the origin as the nearest neighbor distance ( $r$ ) is varied. The removal of the atom at the origin does not affect this calculation, since this atom is stationary with respect to lattice variations, and all the atoms are non-interacting. Figure 1 shows the bulk modulus calculated over changes in nearest

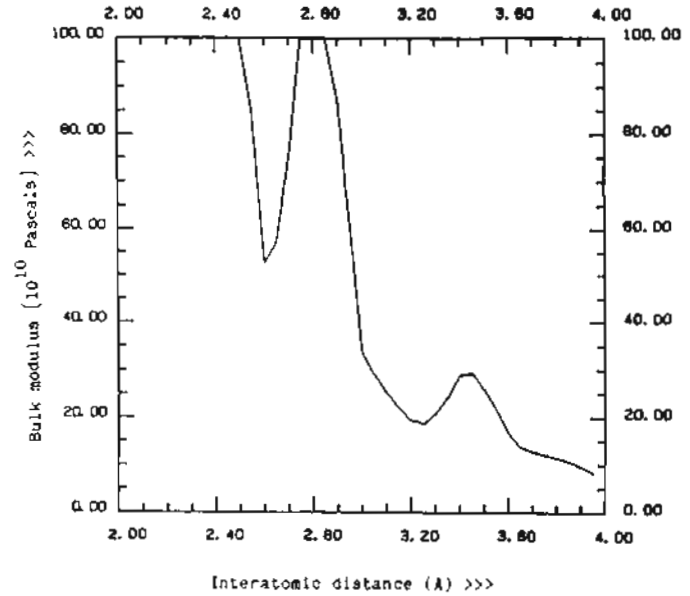


Fig. 1. The predicted bulk modulus over lattice spacing.

neighbor distance. The experimental value for palladium is  $1.87 \times 10^{11}$  pascals [30], whereas the calculated value at  $r = 2.49$  Å is  $5 \times 10^{11}$  pascals, about 2.7 times too high. In other words, this model predicts too stiff a lattice.

The velocity of sound can be similarly calculated. Brillouin [31] gives the following formula for the speed of a wave traveling down a one-dimensional string of particles:

$$v = r \sqrt{\frac{1}{m} \frac{d^2U}{dr^2}} = 953.65 r \sqrt{\frac{d^2U}{dr^2}} \quad (r \text{ in } \text{Å}, U \text{ in e.v.}) \quad (21)$$

From Eq. 10,

$$\frac{d^2U}{dr^2} = -662.39 \left\{ \frac{d^2\phi}{dr^2} - \frac{2}{r} \frac{d\phi}{dr} + \frac{2\phi}{r^2} \right\} \quad (22)$$

Using the solution to the Thomas-Fermi equation (Eq. 9) [25], the predicted velocity of sound is 5,000 m/s, whereas the experimental value is 3,000 m/s [32]. The pressure of the surrounding atoms in the lattice will increase this value so that this model again predicts a lattice that is too stiff.

## ELECTROSTATIC CALCULATIONS OF PALLADIUM

Figure 2 shows the Bravais cube of the palladium lattice along with the path of the electrostatic field plots. The profile of the potential is calculated across the main (4.76 Å) and sub (2.75 Å) diagonals along the face of the primitive cell. Figures 3 and 4 show the potential profiles at the face of the primitive cell; Figs. 5 and 6 show the profiles at the center of the cell. The interesting fact to notice is that the lattice has definite preferred "channels" through which hydrogen can diffuse. Of course, any lattice imperfections will disrupt this flow.

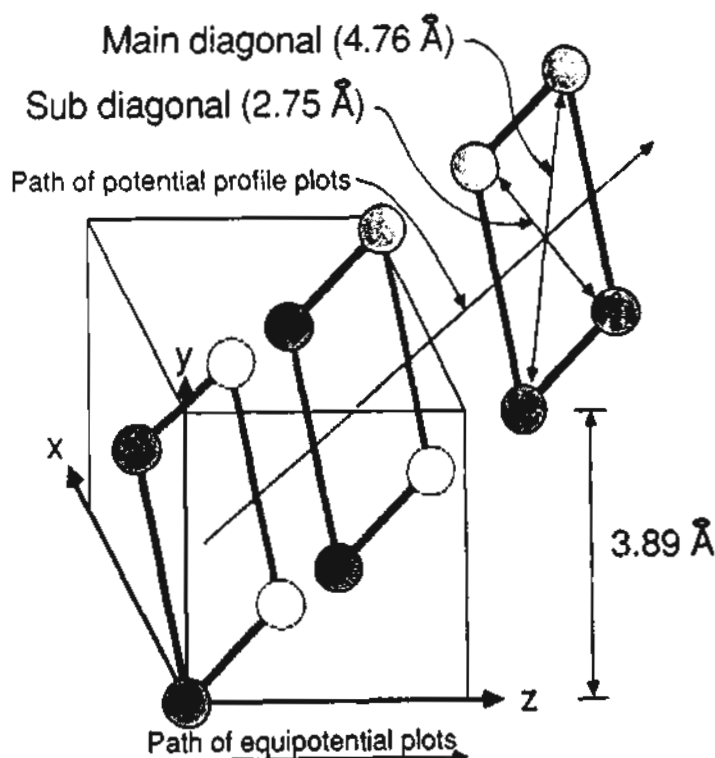


Fig. 2. The Bravais cube showing the primitive cell and the path for subsequent potential plots.

The next series of figures shows the equipotential lines along the Bravais lattice shown in Fig. 2. Figure 7 shows the equipotential lines in the x-y plane at  $z = 0$ . The potential value of the lines is 50 e.v., a convenient value to measure the channel sizes. Figures 8-10 show the same potential lines for  $z = 1, 2,$  and  $3$  Å.

Figures 3-10 show, not surprisingly,

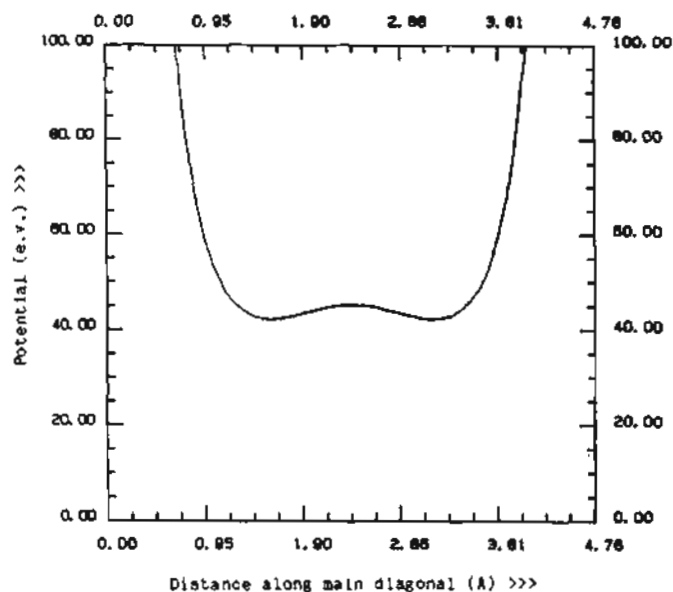


Fig. 3. The potential profile along the main diagonal of the primitive cell.

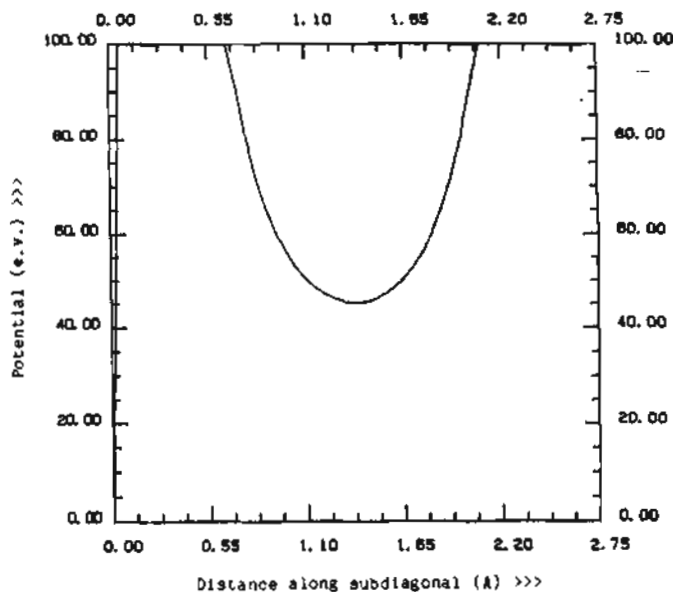


Fig. 4. The potential profile along the subdiagonal of the primitive cell.

that this model predicts palladium to be relatively hard spheres of an approximate diameter of 2.14 Å. This simplification arises from the noninteracting nature of this model; the electron gas is not allowed to redistribute itself to lower the lattice energy. Of course, this model has the advantage of being able to represent actual lattices with their consequent

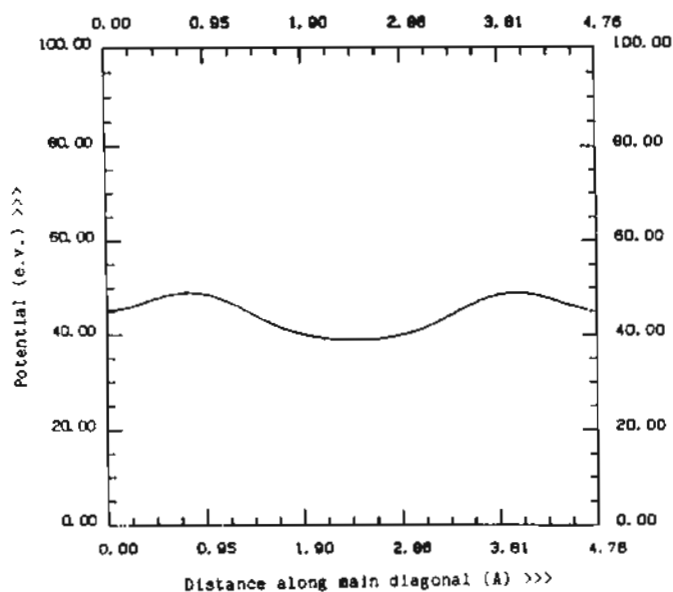


Fig. 5. The potential profile along the main diagonal at the center of the primitive cell.

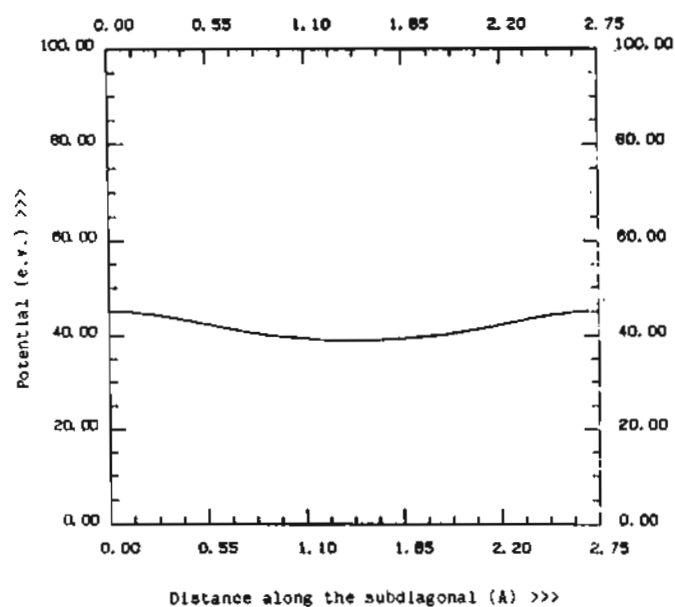


Fig. 6. The potential profile along the subdiagonal at the center of the primitive cell.

defects and impurities. These effects are difficult to model with other methods, such as with SCF calculations [3]. Further, it may be possible to retain the essential simplicity of this model while including the lattice binding through enforcing boundary conditions at the interfaces of the atomic spheres [9].

#### CONCLUSIONS

This paper has presented a prelimi-

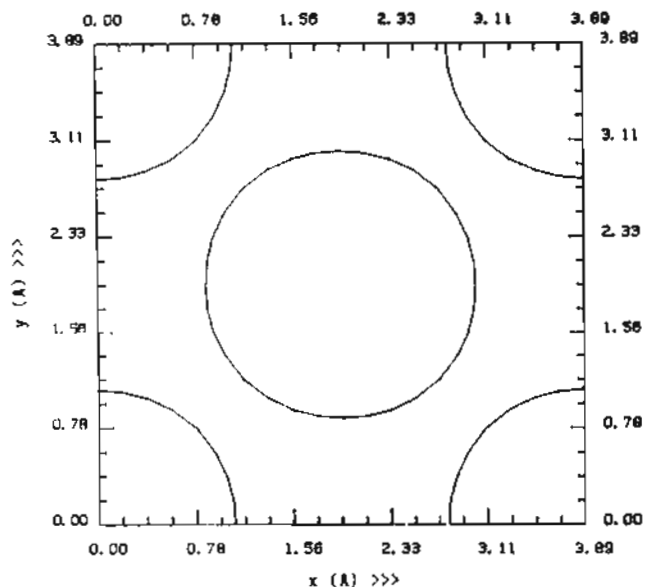


Fig. 7. The equipotential (50 e.v.) lines in the  $x$ - $y$  plane of the Bravais cell for  $z = 0$  Å.

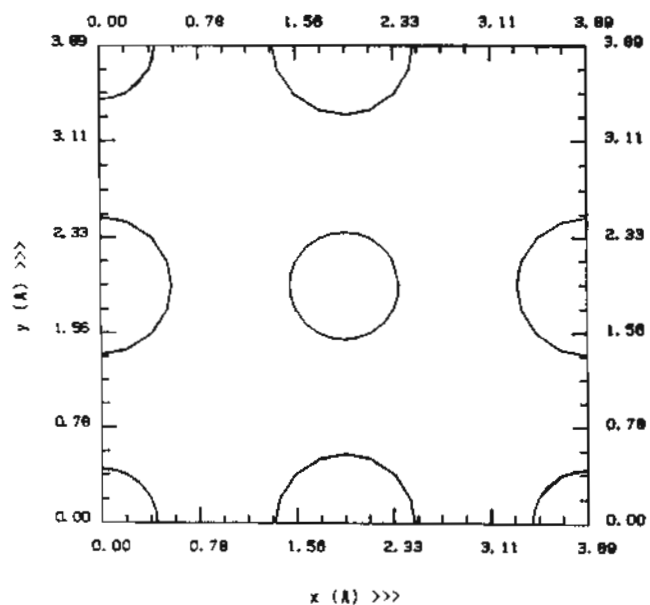


Fig. 8. The same as Fig. 7 for  $z = 1$  Å.

nary investigation into the electrostatic field distribution within the palladium lattice. The palladium atoms are assumed to follow Thomas-Fermi statistics. This approach has the advantage of simplicity as well as the ability to model lattice defects and impurities. The model predicts a lattice that is too stiff for palladium, and it fails to take into account any binding within the material. This model can be used to predict the interaction of hydrogen with palladium showing the locations at which hydrogen can collect and the channels through which hydrogen can flow.

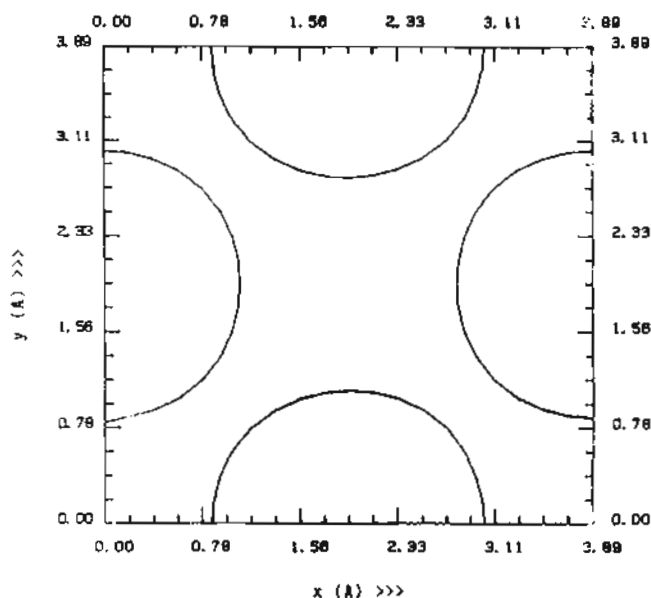


Fig. 9. The same as Fig. 7 for  $z = 2 \text{ \AA}$ .

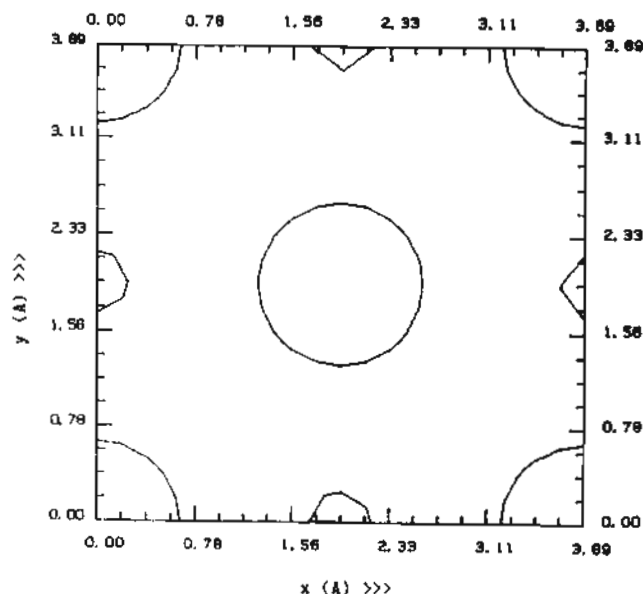


Fig. 10. The same as Fig. 7 for  $z = 3 \text{ \AA}$ .

#### REFERENCES

- [1] F. A. Lewis, The Palladium Hydrogen System, Academic Press, New York, 1967.
- [2] F. D. Peat, Cold Fusion, Contemporary Books, Chicago, Illinois, 1989.
- [3] R. McWeeny, Coulson's Valence, 3rd Edition, Oxford University Press, Fair Lawn, New Jersey, 1979.
- [4] J. C. Slater, Quantum Theory of Molecules and Solids, Vol. 2, McGraw-Hill Book Company, New York, 1965.
- [5] L. H. Thomas, "The Calculation of Atomic Fields," Proceedings of the Cambridge Philosophical Society, Vol. 23, 1927, pp. 542-548.
- [6] E. Fermi, "Eine Statistische Methode zur Bestimmung Einiger Eigenschaften des Atoms und Ihre Anwendung auf die Theorie des Periodischen Systems der Elemente," Zeitschrift fur Physik, Vol. 48, 1928, pp. 73-79.
- [7] L. I. Schiff, Quantum Mechanics, 2nd Edition, McGraw-Hill Book Company, Inc., New York, 1955.
- [8] P. A. M. Dirac, "Note on Exchange Phenomena in the Thomas Atom," Proceedings of the Philosophical Society, Vol. 26, 1930, pp. 376-385.
- [9] N. H. March, "The Thomas-Fermi Approximation in Quantum Mechanics," Advances in Physics, Vol. 6, No. 21, January 1957, pp. 1-101.
- [10] I. H. Lieb and B. Simon, "Thomas-Fermi Theory Revisited," Physical Review Letters, Vol. 31, No. 11, September 1973, pp. 681-683.
- [11] R. Benguria and E. H. Lieb, "Many-Body Atomic Potentials in Thomas-Fermi Theory," Annals of Physics, Vol. 110, 1978, pp. 34-45.
- [12] E. H. Lieb, "Thomas-Fermi and Related Theories of Atoms and Molecules," Reviews of Modern Physics, Vol. 53, No. 4, October 1981, pp. 603-641.
- [13] C. C. J. Roothaan, "New Developments in Molecular Orbital Theory," Reviews of Modern Physics, Vol. 23, No. 2, April 1951, pp. 69-89.
- [14] C. A. Coulson, "Present State of Molecular Structure Calculations," Reviews of Modern Physics, Vol. 32, No. 2, April 1960, pp. 170-177.
- [15] C. C. J. Roothaan, "Self-Consistent Field Theory for Open Shells of Electronic Systems," Reviews of Modern Physics, Vol. 32, No. 2, April 1960, pp. 179-185.

- [16] R. S. Mulliken, "Self-Consistent Field Atomic and Molecular Orbitals and Their Approximations as Linear Combinations of Slater-Type Orbitals," Reviews of Modern Physics, Vol. 32, No. 2, April 1960, pp. 232-238.
- [17] R. K. Nesbet, "Computer Programs for Electronic Wave-Function Calculations," Reviews of Modern Physics, Vol. 35, No. 3, July 1963, pp. 552-557.
- [18] S. M. Blinder, "Basic Concepts of Self-Consistent-Field Theory," American Journal of Physics, Vol. 33, No. 6, June 1965, pp. 431-443.
- [19] J. C. Slater, The Calculation of Molecular Orbitals, John Wiley & Sons, New York, 1979.
- [20] A. Hinchliffe, Computational Quantum Chemistry, John Wiley & Sons, New York, 1988.
- [21] J. Schwinger, "Thomas-Fermi Model: The Leading Correction," Physical Review A, Vol. 22, No. 5, November 1980, pp. 1827-1832.
- [22] J. Schwinger, "Thomas-Fermi Model: The Second Correction," Physical Review A, Vol. 24, No. 5, November 1981, pp. 2353-2361.
- [23] P. Benguria, H. Brezis, and E. H. Lieb, "The Thomas-Fermi-Von Weizsäcker Theory of Atoms and Molecules," Communications in Mathematical Physics, Vol. 79, 1981, pp. 167-180.
- [24] V. C. Aguilera-Navarro, M. de Llano, O. RoJo, and S. L. L. Verardi, "The Thomas-Fermi-Scott-Schwinger Expansion and the Schrödinger Ground State Energy of Complex Neutral Atoms," Journal of Chemical Physics, December 1982, pp. 6131-6133.
- [25] V. Bush and S. H. Caldwell, "Thomas-Fermi Equation Solution by the Differential Analyzer," Physical Review, Vol. 38, November 1931, pp. 1898-1902.
- [26] G. S. Zhdanov, Crystal Physics, Academic Press, New York, 1965.
- [27] E. Teller, "On the Stability of Molecules in the Thomas-Fermi Theory," Reviews of Modern Physics, Vol. 34, No. 4, October 1962, pp. 627-631.
- [28] E. H. Lieb, "The Stability of Matter," Reviews of Modern Physics, Vol. 48, No. 4, October 1976, pp. 553-569.
- [29] W. B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Pergamon Press, New York, 1958.
- [30] C. J. Smithells, Metals Reference Book, 4th Edition, Vols I-III, Plenum Press, New York, 1967.
- [31] L. Brillouin, Wave Propagation in Periodic Structures, 2nd Edition, Dover Publications, Inc., New York, 1946.
- [32] C. J. Smithells, Metals Reference Book, 1st Edition, Butterworths Scientific Publications, London, 1949.