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Relativistic Self-Consistent Field
Calculations for Metallic Cerium *

MASTER

by

J. T. Waber

D. Liberman

and

Don T. Cromer

University of California
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

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ABSTRACT

Relativistic, self-consistent field eigenfunctions for cerium have been obtained which satisfy the two Dirac equations with a potential corrected for exchange by Slater's $\rho^{1/3}$ method and for self-interaction by Latter's method. The solutions were obtained subject to appropriate boundary conditions at the surface of a sphere of radius R . Substantial variation of the eigenvalues with R is observed. The effect of configuration was also studied.

INTRODUCTION

Recently the authors obtained self-consistent relativistic Dirac-Slater wave functions for the free cerium atom. Use of the computer program discussed by Liberman, Waber and Cromer (1) made it feasible to investigate the extent to which the electronic configuration is influenced when the atom is placed in an environment of similar nearby atoms, i.e. when all of the electrons are confined in a sphere of small radius and appropriate continuity conditions at the sphere boundary are applied.

Gschneidner and Smoluchowski (2) have presented a variety of physical and chemical evidence which indicates that metallic cerium at normal density has a single 4f electron localized (and thus part of the ion core) and has 3 electrons presumably arising from the 5d and 6s atomic states. The latter behave as conduction or valence electrons. However, in compression, the normal face-centered cubic gamma phase is transformed to alpha, another face-centered cubic phase, of 1.17 times the normal density. They concluded that on the average only approximately one-half of a 4f electron can be identified as part of the ion core in this collapsed phase. In view of this background of experimental evidence, the effect of compression on the energy levels was investigated.

The Dirac-Slater differential equations were solved subject to appropriate boundary conditions applied at the surface of a sphere. These boundary conditions were different from the conventional Wigner-Seitz boundary conditions (3) because of the nature of the differential equations. Solutions were obtained for four different configurations and for ten different sphere radii R , the two smallest being smaller than the radius

which corresponds to the atomic volume in the collapsed alpha phase.

In addition to following the change of the energy eigenvalues relative to cell radius, the total energy was computed by using the method outlined by Snow, Canfield and Waber.(4) This energy was used to determine which electronic configuration was the most stable for each radius. In this way, evidence supporting an electronic structure change due to compression was obtained. A method of computing the pressure was also investigated.

DESCRIPTION OF THE CALCULATION

Basic Equations

It was assumed that the wave functions of an atom can be presented by a determinant of one-electron wave functions. These were computed by using the approximation for exchange suggested by Slater (5); namely, by replacing the exchange potential with one characteristic of a free electron gas having the local density of a given point in the atom. The direct potential acting on an electron is that of the nucleus and of all the electrons (spherically averaged if there is an unfilled shell). Further details of the model and the method of calculating a self-consistent set of solutions are discussed in the paper by Liberman, Waber and Cromer. (1)

We write the four component Dirac equation in the form

$$\psi(r) = \begin{pmatrix} \frac{1}{r} f(r) i^l \Omega_{jlm} \\ \frac{1}{r} g(r) i^{l'} \Omega_{jl'm} \end{pmatrix} \quad (1)$$

where the Ω 's are two-component normalized spinors with the indicated quantum numbers. The relation between the various quantum numbers may be

conveniently expressed as

$$\begin{aligned}
 l' &= l + s \\
 j &= l + 1/2s = l' - 1/2s \\
 k &= -s (j + 1/2) \\
 s &= \pm 1
 \end{aligned}
 \tag{2}$$

The coupled differential equations for the major $\frac{1}{r} f(r)$ and the minor component $\frac{1}{r} g(r)$ of the radial function may be written in atomic units as

$$\begin{aligned}
 \frac{df}{dr} + \frac{kf}{r} &= \left(\frac{V - E_0 - W}{cs} \right) g \\
 \frac{dg}{dr} - \frac{kg}{r} &= - \left(\frac{V + E_0 - W}{cs} \right) f
 \end{aligned}
 \tag{3}$$

where E_0 is the rest energy of electron, $W = E + E_0$ wherein E is the energy eigenvalue of the (nlj) electron and V is the central potential. In atomic units $\hbar = m = 1$ and the velocity of light $c = 137.037$.

The quantity $rV(r)$, defined as

$$rV(r) = -Z + \int_0^r 4\pi r'^2 \rho(r') dr' + r \int_r^\infty 4\pi r' \rho(r') dr' - Cr \left[\rho(r) \right]^{1/3}
 \tag{4}$$

where Z is the nuclear charge, $\rho(r')$ is the local total electronic charge density and C is $(81/8\pi)^{1/3}$, should approach $N-Z-1$ at large r . However, because Slater's approximation was used, $rV(r)$ will approach $N-Z$. We adopt Latter's suggestion (6) and set $rV(r)$ equal to $N-Z-1$ for all values of the radii greater than r_0 where it first reaches that value. For all but a few of the larger values of cell radius R , r_0 will lie outside the region of interest.

Boundary Conditions

The correct boundary condition for a Dirac electron on the surface of a cell of the crystal lattice is

$$\psi_{\underline{k}}(\underline{r}_1) = e^{i\underline{k} \cdot (\underline{r}_1 - \underline{r}_2)} \psi_{\underline{k}}(\underline{r}_2) \quad (5)$$

where \underline{r}_1 and \underline{r}_2 are two points on the surface which differ by a lattice vector. We shall deal only with the case $\underline{k} = 0$ (assuming that changes in the electron energies for other \underline{k} 's are much the same as for this point in the band when the lattice constant is varied). We will approximate $\psi_0(\underline{r})$ as well as possible by a single term in a spherical harmonic expansion.

With this drastic approximation it is only possible to satisfy the boundary condition at one pair of points. We choose \underline{r}_1 to be a boundary point on a line joining two nearest neighbors in the lattice. Then $\underline{r}_2 = -\underline{r}_1$ and our boundary condition becomes

$$\psi_0(\underline{r}_1) = \psi_0(-\underline{r}_1) \quad (6)$$

The dependence of the major component of the spinor on the angle θ is of even parity if l is even, i.e. $\Omega_{l,jm}$ is an even function of $\cos \theta$, but the dependence of the minor component is odd since $l' = l + s$. That is, the parity of the minor component is opposite that of the major.

The equality in (6) can only be maintained for $\underline{k} = 0$ if

$$\begin{aligned} f(-R_1) = a \text{ and } g_i(R_1) = 0 & \quad l \text{ even} \\ f_i(R_1) = 0 \text{ and } g(R_1) = b & \quad l \text{ odd} \end{aligned} \quad (7)$$

where a and b are constants not defined explicitly here.

Pressure Exerted at the Boundary

The pressure at the boundary has been obtained from the virial function by the method outlined by Hirschfelder, Curtis and Bird. (7) Use of the Dirac equation yields a somewhat simpler derivation than the Schroedinger equation since the former is first order.

The pressure could have been estimated from the slope of the E_T versus R curve, however, the mesh in R was too coarse to obtain accurate values. An expression for the derivative of E_T was derived.

At zero temperature the pressure is given by

$$PV = -V \frac{dW}{dV} \quad (8)$$

For a spherical cell of radius R with $V = 4\pi R^3/3$ we have

$$PV = -(1/3) R \frac{dW}{dR} \quad (9)$$

and

$$W = \int_0^r \psi^*(\underline{r}) \left[\alpha \underline{p} + \beta mc^2 + V(\underline{r}) \right] \psi(\underline{r}) d^3\underline{r} \quad (10)$$

To simplify taking the derivative of the integral, the coordinate \underline{r} is replaced by $R\underline{x}$. Then the limits of integration are fixed. It is also necessary that the normalization of the wave function, regarded as a function of R , be a constant, say unity. From the normalization condition, we have

$$\begin{aligned} R \frac{d}{dR} 1 = 0 &= R \frac{d}{dR} \int_0^1 \psi^*(R\underline{x}, R) \psi(R\underline{x}, R) R^3 d^3\underline{x} \\ &= 3 + \int_0^1 (\underline{r} \cdot \underline{\nabla} + R \frac{\partial}{\partial R}) |\psi(\underline{r}, R)|^2 d^3\underline{r} \end{aligned} \quad (11)$$

The derivative of the energy is

$$\begin{aligned}
 R \frac{dW}{dR} &= R \frac{dW}{dR} \int_0^1 \psi^* (R\underline{x}, R) \left[c\underline{\alpha} \cdot \frac{\hbar}{iR} \nabla_{\underline{x}} + \beta mc^2 + V(R\underline{x}) \right] \psi(R\underline{x}, R) R^3 d^3\underline{x} \\
 &= 3W + W \int_0^R (\underline{r} \cdot \nabla + R \frac{\partial}{\partial R}) |\psi(\underline{r}, R)|^2 d^3\underline{r} \\
 &\quad + \int_0^R \psi^*(\underline{r}) \left[-c\underline{\alpha} \cdot \underline{p} + \underline{r} \cdot \nabla V(\underline{r}) \right] \psi(\underline{r}) d^3\underline{r} \quad (12)
 \end{aligned}$$

Comparing the first two terms with the derivative of the normalization condition shows that their sum is zero. Only the last term must be dealt with and it can be reduced to a surface integral.

Above, it was assumed that $V(\underline{r})$ has no dependence on the cell size other than that introduced by the substitution of $R\underline{x}$ for \underline{r} . This is not true for the potential in a self-consistent field calculation such as this one. However, the same result is obtained for either the exact many-body problem or the Hartree-Fock approximation, except for a small additional term due to the inhomogeneities of the total charge distribution. Neglecting this term is equivalent to neglecting the contribution to the potential within a cell in a crystal lattice of the charges outside the cell.

The next step is to reduce the remaining volume integral to a surface integral. Starting from the identity

$$\psi^* \underline{r} \cdot \nabla (H\psi) - (H\psi)^* \underline{r} \cdot \nabla \psi \equiv 0 \quad (13)$$

some manipulation gives

$$\psi^* (-c\underline{\alpha} \cdot \underline{p} + \underline{r} \cdot \nabla V) \psi = -\nabla \cdot c \left[\psi^* \underline{\alpha} (\underline{r} \cdot \underline{p}) \psi \right] \quad (14)$$

Combining the results of equations (9), (12), and (14) gives the desired result:

$$PV = 1/3 \int \psi^* (c\underline{\alpha} \cdot \underline{n} (\underline{r} \cdot \underline{p}) \psi) dS \quad (15)$$

\underline{n} is a unit vector normal to the surface of the cell.

For spherical cells, a further reduction is possible. Here $\underline{n} = \underline{r}/r$.

We multiply both sides of the well known identity

$$(\underline{\alpha} \cdot \underline{r}) (\underline{\alpha} \cdot \underline{p}) = \underline{r} \cdot \underline{p} + i \underline{\sigma} \cdot \underline{r} \times \underline{p} \quad (16)$$

by $\underline{\alpha} \cdot \underline{n}$. Use of $\underline{L} = \underline{r} \times \underline{p}$ and the Dirac equation gives

$$c \underline{\alpha} \cdot \underline{nr} \cdot \underline{p} \psi = r (W - V - \beta mc^2) \psi - ic (\underline{\alpha} \cdot \underline{n}) (\underline{\sigma} \cdot \underline{L}) \psi \quad (17)$$

so that

$$PV = 1/3 \int \psi^* \left[r (W - V - \beta mc^2) - ic (\underline{\alpha} \cdot \underline{n}) (\underline{\sigma} \cdot \underline{L}) \right] \psi dS \quad (18)$$

Inserting the terms in (18) and integrating, one obtains the result for the i^{th} electron

$$(PV)_i = \left\{ \left[f_i(R)^2 + g_i(R)^2 \right] \left[W_i R + Z - RV(R) \right] + 2 \left[cR g_i(R)^2 - (2j + 1) c f_i(R) g_i(R) \right] \right\} / 3 \quad (19)$$

The total pressure

$$P_T = \frac{1}{V} \sum (j) (PV)_j q_j \quad (20)$$

was used in the results discussed below.

RESULTS AND DISCUSSION

The variations of some of the energy eigenvalues for the $4f^1 5d^1 6s^2$ configuration are shown in Fig. 1 where they are plotted vs the reciprocal of the sphere radius, R . These values correspond to $k = 0$ in equation (5), or the bottom of the energy band. The curves for the top of the band would rise much more rapidly and would exhibit no minima. The points corresponding to the Wigner-Seitz radii of γ and α -cerium are indicated in Fig. 1. The point is also marked at which the maximum in the total energy occurs for this configuration (cf Fig. 3).

The variation of three of the energy eigenvalues and the total energy with electronic configuration is shown in Fig. 2. The values are for the sphere radius of 3.811 a.u., the Wigner-Seitz radius for normal or γ -cerium. The general trend of these relativistic Dirac-Slater eigenvalues with x , the number of f electrons, is similar to that shown by Waber and Larson (8) who used non-relativistic Hartree eigenvalues for the free cerium atom. The variation of the total energy curve suggests that there is a little more than one $5d$ electron in γ -cerium.

The variation of total energy with sphere radius is shown in Fig. 3. For a free cerium atom, i.e. in the present case, one confined to a sphere of radius 60.0 Bohr units (37.75 Å), the ground state is $4f^1 5d^1 6s^2$. Up to the density corresponding to γ -cerium this is the most stable state. However, on further compression the total energy for the configuration $4f^{0.5} 5d^{1.5} 6s^2$ is lower and this configuration is the most stable state. This trend is in substantial agreement with the deductions of Gschneidner and Smoluchowski (2). These deductions were based primarily on magnetic

susceptibility data and on the variation of the experimental atomic radii of the elements with the number of valence electrons which Zachariassen (9) has observed. It is predicted that on further compression the ground state would become $5d^26s^2$.

The one-electron radial density function ($f_1^2 + g_1^2$) is shown in Fig. 4 for $R = 3.811$ and the configuration $4f^15d^16s^2$. The abscissa is a logarithmic scale of r . The maxima in the individual density curves correspond approximately to maxima or minima in the major component $\frac{1}{r} f(r)$. The effects of the r multiplier and the minor component are to shift the maxima in the density curve (generally) to the right.

The probability of finding a $6s$ or $5d$ electron at the boundary of the sphere is large in comparison with the corresponding probability of finding the $4f$ electron. These quite different probabilities are of course a consequence of the boundary conditions that have been imposed. For the $4f$ electrons, because l is odd, the major component must be zero. The minor component must be non-zero but in any event it will be small. For the $6s$ and $5d$ electrons l is even and the major component is non-zero. The value of the major component can become quite large at the boundary because of the normalization condition, and, as compression increases, the boundary values of these major components become larger and larger.

The single electron density functions obtained from non-relativistic Hartree wave functions for the free cerium atom have been given by Waber and Larson (8). In this case, even though the Wigner-Seitz or the present boundary conditions do not apply, the $4f$ density is vanishingly small at radii larger than 3.811 a.u. In contrast, the $5d$ and $6s$ densities for the

free atom are significantly larger than the 4f density in this region. In fact, the principal maximum of the 6s density lies beyond the Wigner-Seitz radius in the two configurations studied by Waber and Larson (8). This observation lends support to the idea that the 4f electrons are localized near the atomic nucleus and do not contribute significantly to metallic conduction.

In Fig. 5 the total pressure is plotted vs $1/R$ for the $4f^1 5d^1 6s^2$ configuration. The pressure starts out at zero for the free atom and, as compression occurs, the pressure becomes slightly negative, an indication of the tendency for free cerium atoms to coalesce. The pressure has a small shallow minimum, on further compression, and then rises rapidly to cross the line of zero pressure at essentially the same radius at which the minimum in total energy occurs. These curves for other configurations are very similar.

Waber and Larson (8) have estimated the cohesive energy and the equilibrium radius of cerium by using the relatively simple Fröhlich-Raimes method (10,11,12). They found the equilibrium radius for trivalent cerium to be 4.46 a.u. and that for tetravalent cerium to be 3.49 a.u. It is interesting that the present treatment leads to a similar value for the $4f^1 5d^1 6s^2$ configuration. The Fröhlich-Raimes estimate of the cohesive energy or heat of sublimation is -10 for trivalent and 348 kcal/mol for tetravalent cerium. The present calculation (obtained from the difference between the free atom total energy and the minimum total energy cf. Fig. 3) yields 129 kcal/mol for the $4f^1 5d^1 6s^2$. The experimental value (13) is 97.9 kcal/mole. Thus the present calculation is a significant improvement over the Fröhlich-Raimes method for the heat of sublimation.

We show, in Fig. 6, the X-ray scattering factor for four sizes of the $4f^26s^2$ configuration. In the low $\sin \theta/\lambda$ region, f increases as R decreases, and the difference between the scattering factors for γ cerium and the free atom is nearly 0.7 electron in some regions. In crystal structure work with cerium metal, or cerium alloys, it might be more appropriate to use the scattering factor for the compressed atom than that for the free atom. The four curves in Fig. 6 gradually converge and are essentially identical for $\sin \theta/\lambda > 0.3$.

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CAPTIONS

- Fig. 1. The effect of compression on the energy eigenvalues for various orbitals of the cerium atom confined in a sphere of radius R . The (nlj) quantum numbers are indicated for each electronic level. The symbols γ and α indicate the Wigner-Seitz radius of the gamma and alpha phases of metallic cerium.
- Fig. 2. Effect of the number of f electrons in the general configuration $6s^2 5d^{2-x} 4f^x$ on the energy eigenvalues of various electron levels and the total energy. The sphere radius used corresponds to the normal density of cerium metal.
- Fig. 3. Effect of compression and electronic configuration on the total energy of confined cerium atoms. The j quantum numbers are not indicated in this figure.
- Fig. 4. Plot of the radial density function for a single electron ($f_i^2 + g_i^2$). For a cerium atom ($4f^1 5d^1 6s^2$) in a sphere of radii equivalent to that for gamma cerium.
- Fig. 5. Total pressure vs $1/R$ for the configuration $4f^1 5d^1 6s^2$.
- Fig. 6. X-ray scattering factors for four sizes of the $4f^2 6s^2$ configuration of cerium.

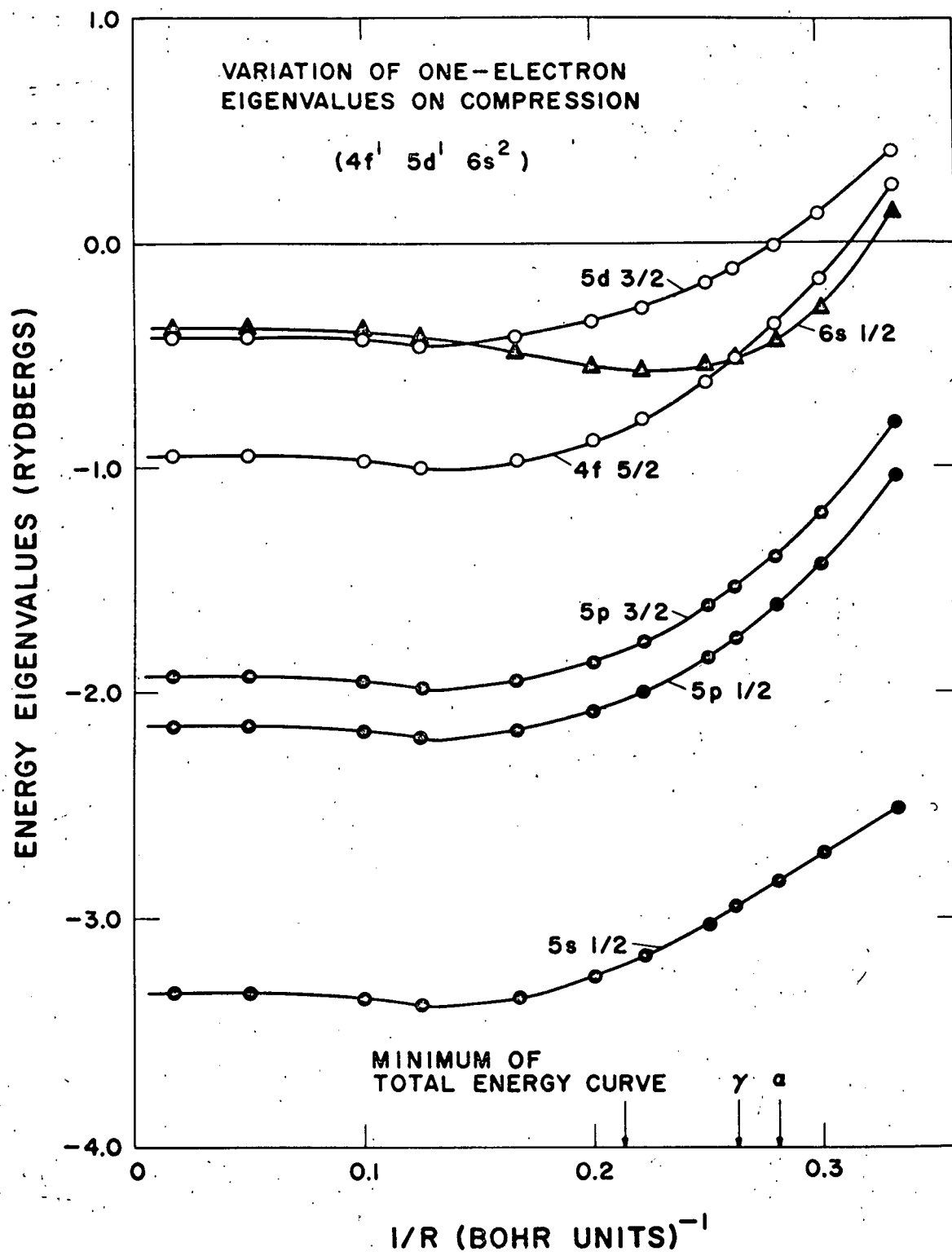


Figure 1

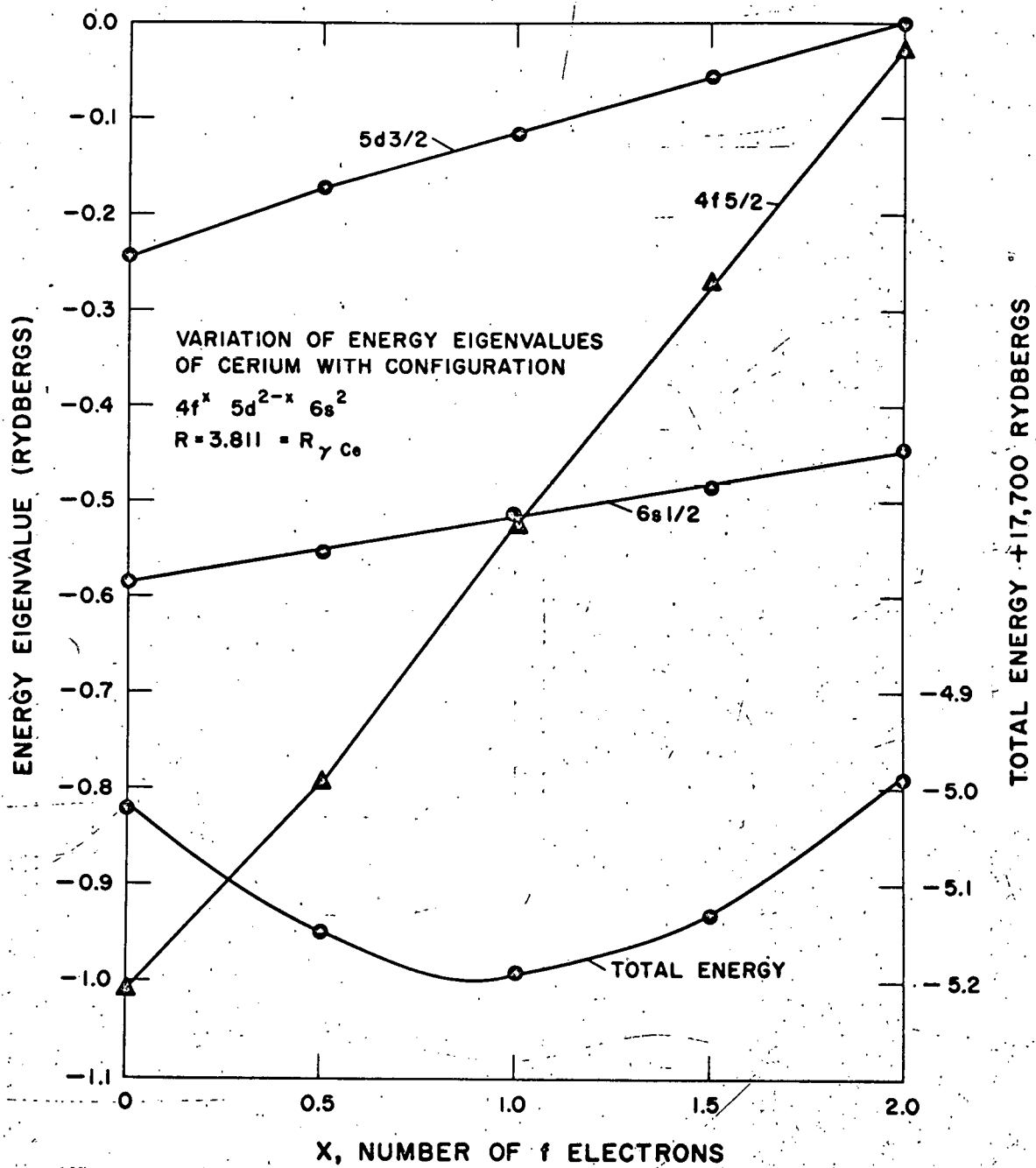


Figure 2

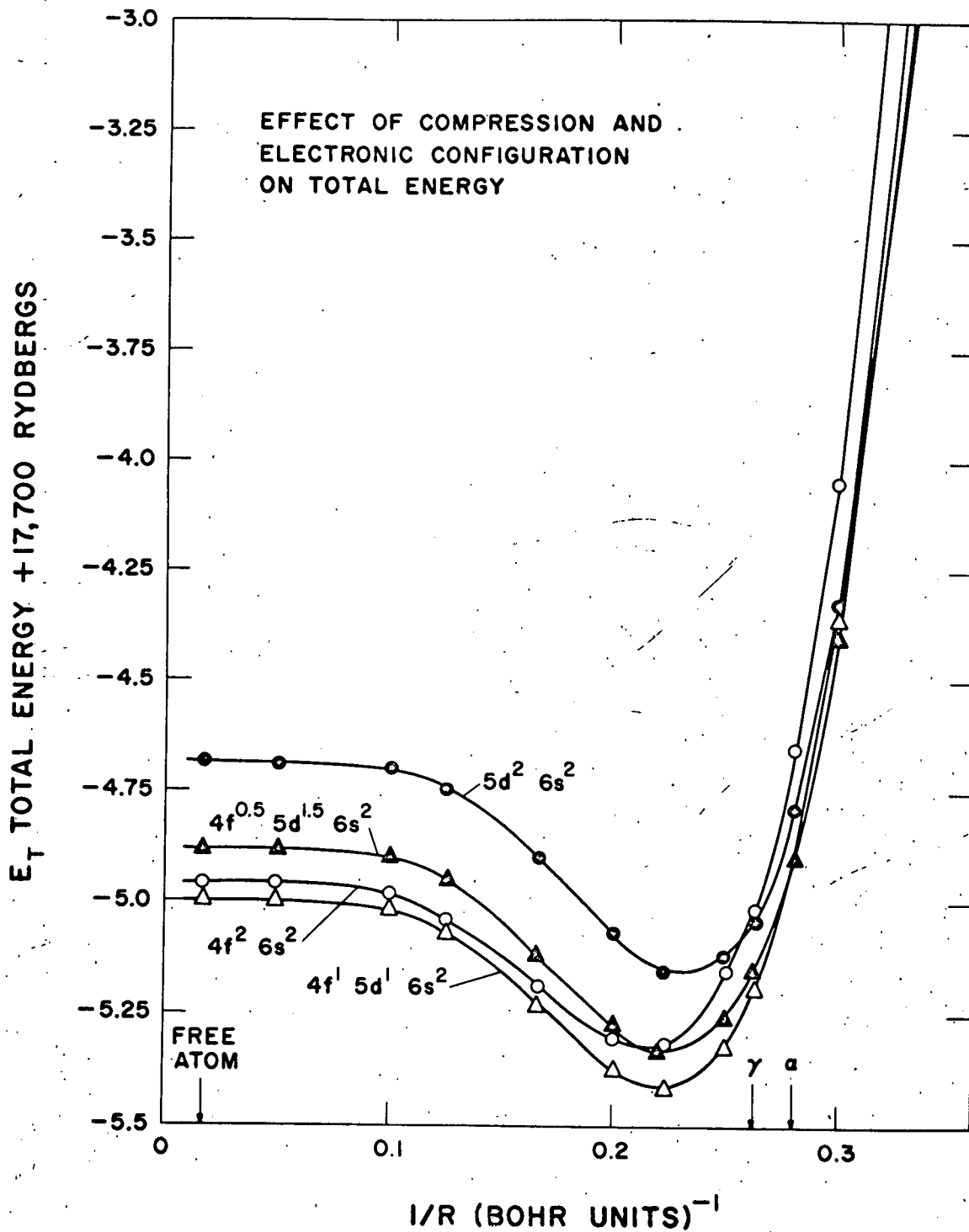


Figure 3.

SINGLE-ELECTRON RADIAL
DENSITY FUNCTION ($f_1^2 + g_1^2$)

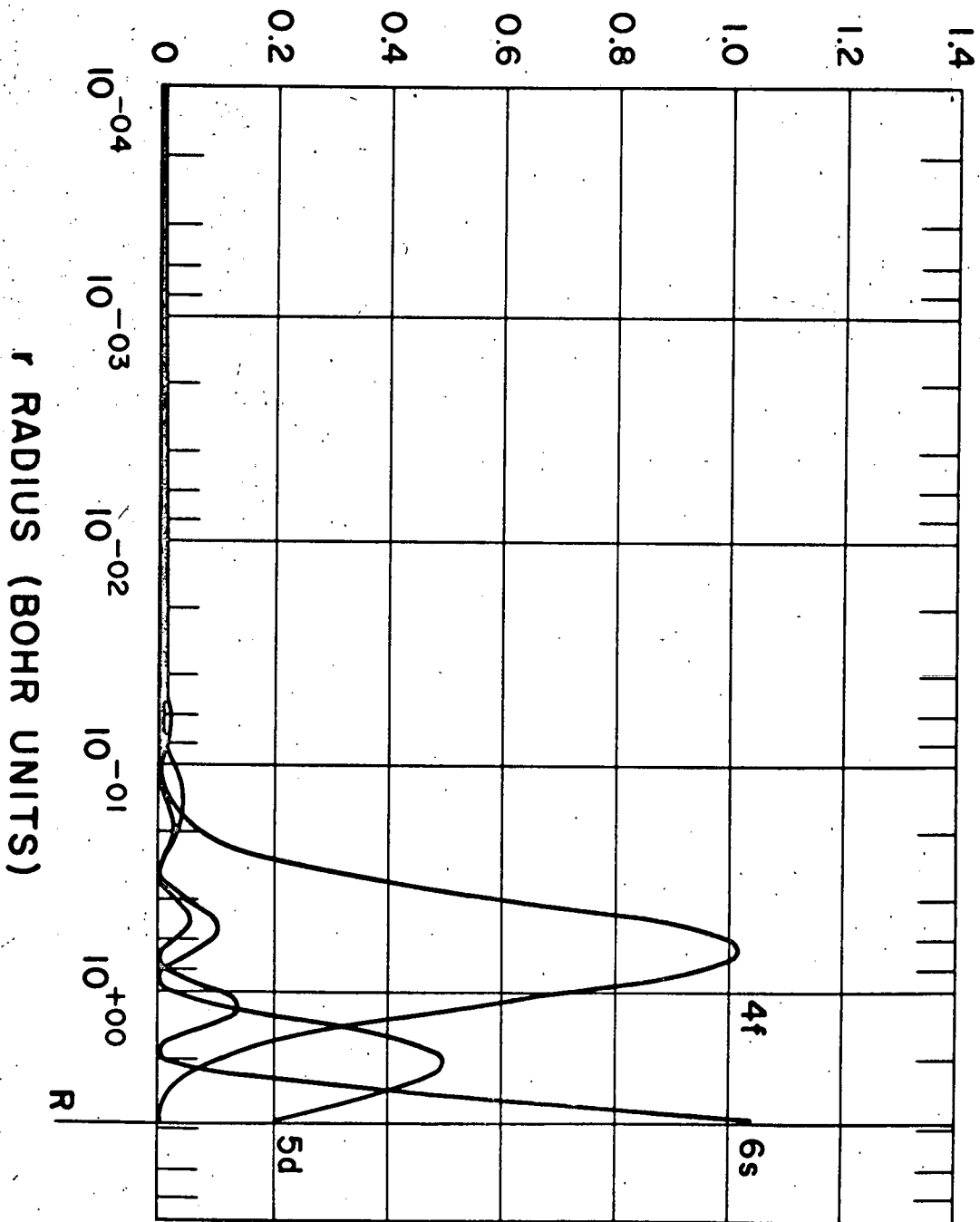


Figure 4

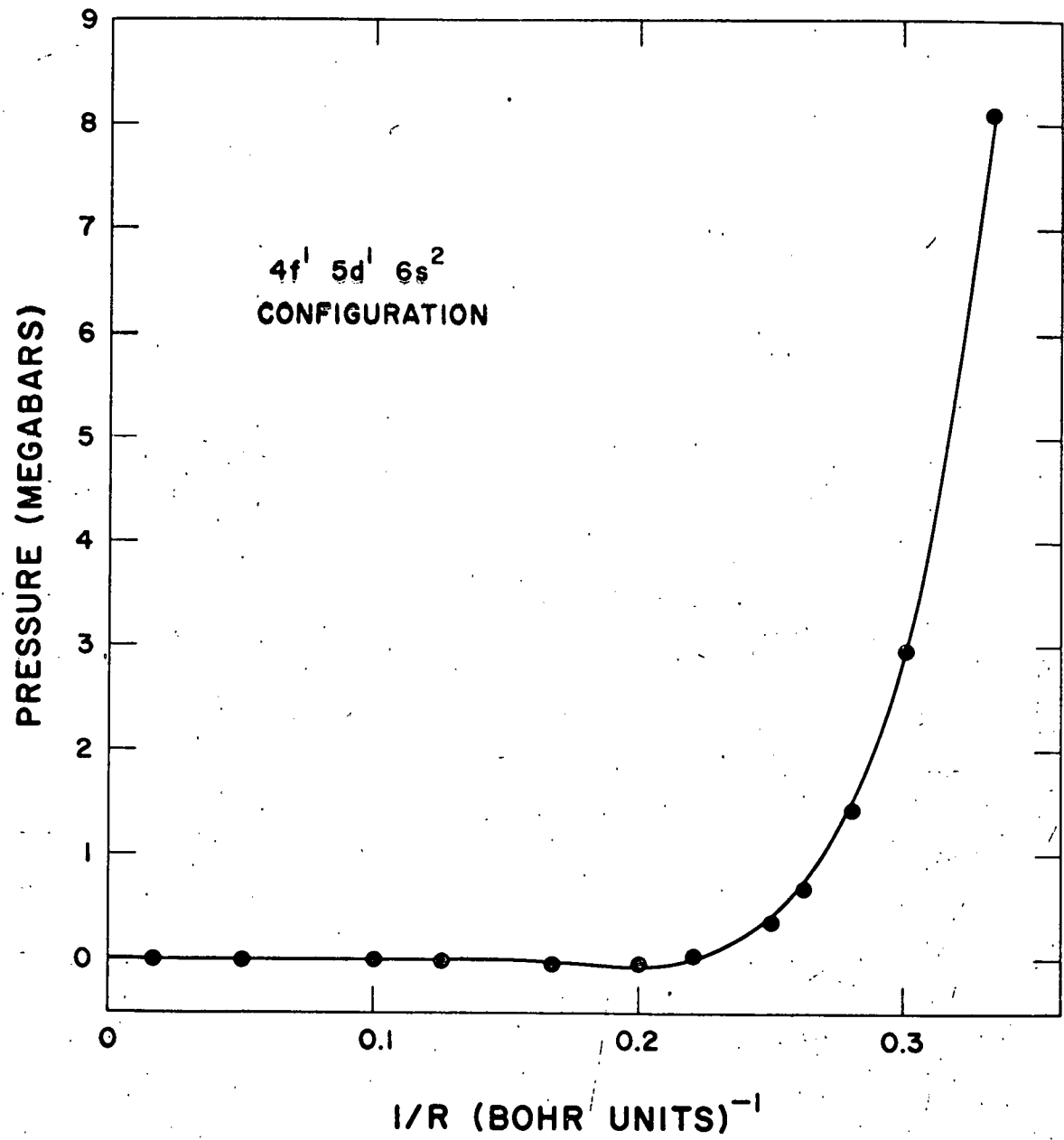


Figure 5

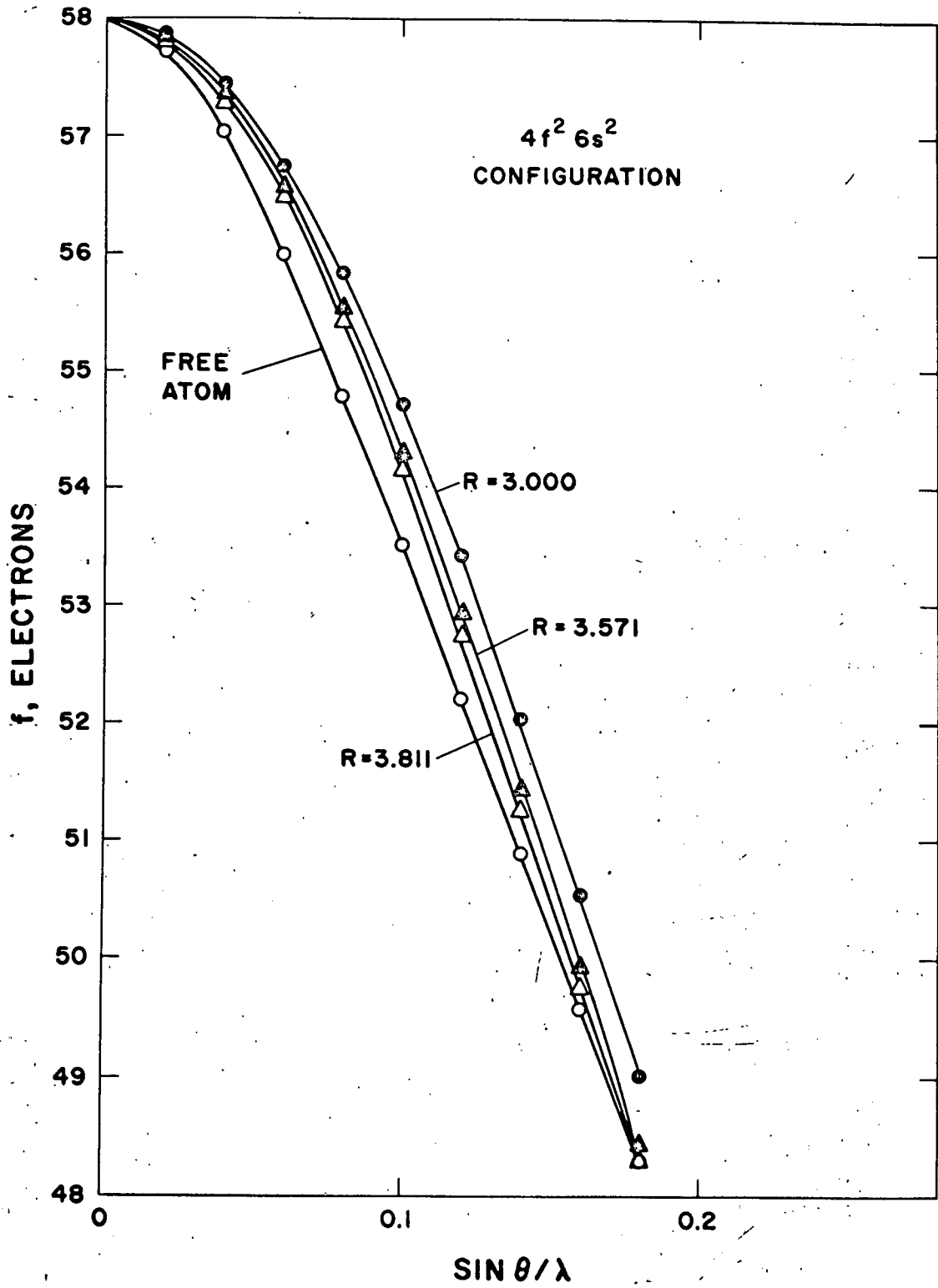


Figure 6