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Atomic vibrations in a self-consistent-field atom-in-jellium model of condensed matter

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The electronic structure of many of the elemental solids is fairly well represented by a single atom embedded in a degenerate electron gas. This is particularly true for bulk properties such as the equation of state of highly compressed matter. Because the atom-in-jellium model is spherically symmetric, it is simpler than band-structure models. We study what happens when the nucleus is moved off center in the atomic cell to form a nonspherical system. This forms the basis of an Einstein model of atomic vibrations. The model is used to calculate Einstein temperatures and Grüneisen constants of simple solids by self-consistent-field electronic-structure methods.

I. INTRODUCTION

With the advent of modern computers, excellent calculations of zero-temperature equations of state of many simple solids have been made using self-consistent-field (SCF) methods.[1-4] Errors in estimates of the solid densities at zero pressure are usually not more than a few percent. Since SCF band-structure computations are rather complex, less has been done than might be desired in extending these calculations to complex crystals, to high-Z elements (where relativity plays an important role), and to nonzero temperatures. About ten years ago an atom-in-jellium model[5-7] was devised to make some progress with high-temperature equations of state and to study high-Z materials under compression. The results were quite encouraging: there was only a modest loss of accuracy as compared to band-structure calculations, and the simplicity and ease of the calculations made it possible to compute thermal contributions to equations of state for materials containing either low- or high-Z atoms. One thing was missing though; at low temperatures atomic vibrations dominate the specific heat and the model contains only the electronic excitation contribution. This paper addresses the problem of atomic vibrations within the atom-in-jellium model.

II. THE ATOM-IN-JELLIUM MODEL

The simplest qualitative model of a metal is the uniform degenerate electron gas. Coulomb interactions are assumed, but these are largely canceled by a uniform positive charge background which exactly neutralizes the electron gas. This construct is called a *jellium*. Either many-body quantum mechanics or self-consistent-field methods can be applied in studying the properties of the jellium.

A more useful model of solids is a periodic array of nuclei with a neutralizing bath of electrons. Ordinarily self-consistent-field methods are used to describe the electron states. This model has been very successful in describing many properties of solids including cohesive energy and zero-temperature equations of state. We refer to it as the band structure model. The self-consistent-field procedure most commonly used in band-structure calculations is the local density approximation devised by Kohn and Sham.[8] We use it in our calculations along with the Gunnarson-Lundquist[9] expression for the exchange-correlation energy density.

A third model lying somewhere between these two is the atom-in jellium[5]—a single atom embedded in a jellium. It has much of the simplicity of an isolated atom but captures much of the physics of the band-structure model. In particular it also does a pretty good job of describing cohesion and the behavior of solids under compression. Its simplicity has made it attractive for calculations of heavy atoms where the Dirac equation should be used and for high-temperature equations of state.

The atom-in-jellium model is depicted in Fig. 1. An infinite positive charge distribution has a cavity at the center of which is a single nucleus. There are sufficient electrons to neutralize both the nucleus and the surrounding positive charge. An additional constraint is imposed: The atomic cavity contains enough electrons to neutralize the nucleus, and the region outside is also electrically neutral. Again the electrons are governed by quantum mechanics. In our case a set of SCF one-electron Dirac equations are used.

Finally, we come to the main point of this paper: the Einstein oscillator model of atomic vibrations.[10] Imagine now that the nucleus at the center of the atomic sphere is moved off center by a small amount x. The energy of the system is changed by the amount $E_2=\frac{1}{2}Kx^2$, and the nucleus "feels" a restoring force $F_2=-Kx$. K is the Hooke's law constant. The change in energy E_2 will be calculated from a perturbation treatment of the electronic structure equations (the SCF one-electron Dirac equations mentioned in the preceding paragraph). E_2 is then used as the potential term in the Schrödinger equation for nuclear motion. This Schrödinger equation is that of a harmonic oscillator. It is well known that the Einstein

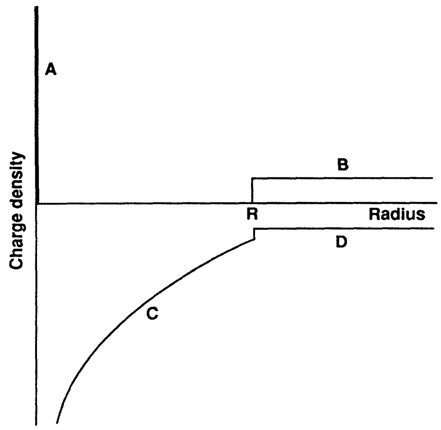

FIG. 1. A schematic charge distribution for the atom-in-jellium model: *A*, a point nucleus at the center of a spherical cavity; *B*, a constant positive charge density outside the cavity which represents surrounding ions; *C*, a spherically symmetric electronic charge density inside the cavity. *D*, a volume averaged electronic charge density outside the cavity. *R* is the radius of the cavity (or atomic sphere) which is electrically neutral. The outside region is also neutral.

oscillator frequency, ω, can be defined by $K=M\omega^2$, where M is the nuclear mass. The Einstein temperature, Θ_E, is defined by $k_B\Theta_E=\hbar\omega$ where k_B is the Boltzmann constant.

We now want to alter the picture drawn in the preceding paragraph slightly. When the nucleus is moved off center as described, the perturbation resulting is rather singular, and there is some chance of mathematical difficulty either analytic or numerical. Instead suppose that the nucleus is fixed and the positive charge outside the atomic cavity is rigidly displaced by the amount x. This is completely equivalent. The perturbation now takes the form of a dipole layer on the surface of the atomic sphere. E_2 will be calculated for that perturbation.

III. THE MATHEMATICAL DESCRIPTION

The energy functional whose minimum constitutes the solution of the problem will now be specified. The potential energy part of it depends on the charge densities. The positive charge density is

$$\rho_+(\mathbf{r})=Z\delta(\mathbf{r})+\sigma(\mathbf{r})\ , \tag{1}$$

where $\sigma(\mathbf{r})=\bar{\rho}\ \Theta(r-R)$ and $\Theta(r-R)$ is the Heaviside unit-step function. The positive charge background of the jellium has a cavity of radius R; otherwise it is constant. The negative charge density is

$$\rho_-(\mathbf{r})=\textstyle\sum_i n_i|\psi_i(\mathbf{r})|^2\ . \tag{2}$$

There are bound and continuum parts to $\rho_-(\mathbf{r})$. The occupation factors, n_i, are (in the zero-temperature case) one or zero for one-electron states with energy less than or greater than the Fermi energy. The value of $\rho_-(\mathbf{r})$ at very large radius is

$$\rho_-(\infty)=\int\frac{d\mathbf{k}}{(2\pi)^3}2n_k=k_F^3/(3\pi^2)=\bar{\rho}\ , \tag{3}$$

where k_F is the Fermi wave number.

To simplify the model somewhat a "muffin-tin" charge density[11] is also defined:

$$\rho(\mathbf{r})=\rho_-(\mathbf{r}),\quad r<R\ : \tag{4a}$$

and

$$\rho(\mathbf{r})=\int_{x>R}\rho_-(\mathbf{x})d\mathbf{x}\bigg/\int_{x>R}d\mathbf{x},\quad r>R\ . \tag{4b}$$

Outside the atomic sphere the Friedel oscillations and exponential tails of the bound states in $\rho_-(\mathbf{r})$ are averaged out in $\rho(\mathbf{r})$, and we are left with a constant which is $\rho_-(\infty)$.

The atom-in-jellium system must be electrically neutral. We *impose* local neutrality by requiring

$$\int_{r<R}\rho(\mathbf{r})d\mathbf{r}=Z\ . \tag{5}$$

This is a constraint on the system and is introduced into the energy functional with a Lagrange multiplier. Equation (5) is satisfied either by adjusting the cell radius R or the Fermi energy E_F.

The kinetic-energy part of the energy functional is

$$K=\sum_i n_i\int\psi_i^*[c\boldsymbol{\alpha}\cdot\mathbf{p}+mc^2(\beta-1)]\psi_i d\mathbf{r} \tag{6}$$

and the potential-energy part is

$$\begin{aligned}V=&-\int Ze^2[\rho(\mathbf{r})-\sigma(\mathbf{r})]/r\,d\mathbf{r}\\&+\tfrac{1}{2}\int\int e^2[\rho(\mathbf{r})-\sigma(\mathbf{r})]\\&\qquad\times[\rho(\mathbf{r}')-\sigma(\mathbf{r}')]/|\mathbf{r}-\mathbf{r}'|d\mathbf{r}\,d\mathbf{r}'\\&+\int\rho(\mathbf{r})\varepsilon_{xc}[\rho(\mathbf{r})]d\mathbf{r}\ .\end{aligned} \tag{7}$$

The potential energy is written as a functional of the muffin-tin charge density, Eq. (4), but depends through Eq. (2) on the orbital functions, $\psi_i(\mathbf{r})$. V contains Coulomb terms and an exchange-correlation energy as well.

The total energy of the system, $E=K+V$, is minimized subject to orbital normalization constraints and the electrical neutrality requirement in the usual fashion: we write

$$J[\psi_i;R]=K+V-\nu\int_{r<R}\rho d\mathbf{r}-\sum_i\lambda_i\int|\psi_i|^2d\mathbf{r} \tag{8}$$

and demand that

$$\frac{\delta J}{\delta\psi_i^*}=0 \tag{9}$$

and

$$\frac{\partial J}{\partial R}=0\ . \tag{10}$$

From Eq. (9) the one-electron equations follow:

$$[c\boldsymbol{\alpha}\cdot\mathbf{p}+mc^2(\beta-1)+v(\mathbf{r})-\varepsilon_i]\psi_i(\mathbf{r})=0\ , \tag{11}$$

where $\varepsilon_i = \lambda_i / n_i$ are the energy eigenvalues and the potential function is

$$v(\mathbf{r}) = -Ze^2/r + \int_{r'<R} e^2\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|\,d\mathbf{r}' + v_{xc}(\rho(\mathbf{r})) - \nu \tag{12a}$$

for $r<R$ and

$$v(\mathbf{r}) = v_{xc}[\rho(\infty)] \tag{12b}$$

for $r>R$. $v_{xc}(\rho)$ is the exchange-correlation potential

$$v_{xc}(\rho) = \frac{\partial}{\partial\rho}\varepsilon_{xc}(\rho) \ . \tag{13}$$

ν derives from Eq. (10) and is

$$\begin{aligned}\nu = \{&\rho(R)\varepsilon_{xc}[(\rho(R)] - \rho(\infty)\varepsilon_{xc}[\rho(\infty)] \\ &+ v_{xc}[\rho(\infty)][\rho(\infty)-\rho(R)]\}/\rho(R) \ .\end{aligned} \tag{14}$$

Both bound and continuum solutions to the one-electron equations, (11), exist; both contribute to the electron charge density. The bound orbitals decay exponentially outside the atomic sphere and are normalized to unity:

$$\int_{r<\infty} |\psi_i(\mathbf{r})|^2 d\mathbf{r} = 1 \ . \tag{15}$$

For the continuum orbitals, a convenient normalization is

$$\int_{r<\infty} \psi^*_{kJ}(\mathbf{r})\psi_{k'J'}(\mathbf{r})\,d\mathbf{r} = \frac{\pi}{2kk'}\delta(k-k')\delta_{JJ'} \ , \tag{16}$$

where J and J' are angular momentum quantum numbers and k and k' are Fermi wave numbers. Outside the atomic sphere the potential function is constant, and there are analytic forms for the orbital functions. Inside the atomic sphere numerical integration of the Dirac equation determines the orbital functions. In the continuum, we use a special interpolation procedure which is described in the Appendix. It is accurate, fast, and well adapted to dealing with resonances which occur frequently.

We want to use the atom-in jellium model to obtain information about atoms in condensed matter—that is atoms surrounded by other atoms. As explained in Ref. 5 we have tried various ways of extracting information from our model which will approximately separate the contributions of the atom and the surrounding jellium. We found empirically that the best scheme was simply to truncate expectation values for relevant physical quantities at the atomic sphere boundary. Thus the atomic kinetic energy is

$$K_A = \sum_i n_i \int_{r<R} \psi^*_i(\mathbf{r})[c\boldsymbol{\alpha}\cdot\mathbf{p} + mc^2(\beta-1)]\psi_i(\mathbf{r})\,d\mathbf{r} \ ; \tag{17}$$

and the potential-energy contribution is

$$\begin{aligned}V_A = &-\int_{r<R} Ze^2\rho(\mathbf{r})/r\,d\mathbf{r} \\ &+ \tfrac{1}{2}\int_{r,r'<R}\int e^2\rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|\,d\mathbf{r}\,d\mathbf{r}'\end{aligned} \tag{18}$$

The density of states in the continuum is

$$g_A(E) = \sum_J \int_{r<R} |\psi_{kJ}(\mathbf{r})|^2 d\mathbf{r} \ . \tag{19}$$

Equations (17)–(19) are consistent with results of Anderson and McMillan.[12]

When the positive charge background of the jellium is moved off center, the energy functional $E=K+V$ remains the same except that the charge density σ of the jellium becomes

$$\sigma(\mathbf{r}) = \bar{\rho}\Theta(|\mathbf{r}-\mathbf{x}|-R) \ , \tag{20}$$

which for small displacements $\mathbf{x}$ is

$$\begin{aligned}\sigma(\mathbf{r}) = \bar{\rho}[&\Theta(r-R) - x\mu\delta(r-R) + \tfrac{1}{2}x^2(1-\mu^2)\delta(r-R)/\mathbf{r} \\ &+ \tfrac{1}{2}x^2\mu^2\delta'(r-R) + \cdots] \\ = {}&\sigma^0(\mathbf{r}) + x\sigma^1(\mathbf{r}) + x^2\sigma^2(\mathbf{r}) + \cdots \ ,\end{aligned} \tag{21}$$

where μ is the cosine of the angle between $\mathbf{r}$ and $\mathbf{x}$ and δ and δ' are the Dirac delta function and its derivative. Since the change in E to second order in x will be calculated, there is a chance that σ_2 and other second-order terms will be needed.

In shifting the positive charge background off center, we have chosen not to do the same with the neutrality constraint, Eq. (5).

As in the original spherically symmetric case, a functional J is formed from the total energy expression and the constraints, and the functional is varied to find its minimum. A set of one-electron equations is obtained.

$$(h-\varepsilon_i)\psi_i(\mathbf{r}) = 0 \ , \tag{22}$$

where

$$h = c\boldsymbol{\alpha}\cdot\mathbf{p} + mc^2(\beta-1) + v(\mathbf{r}) \tag{23}$$

and

$$\begin{aligned}v(\mathbf{r}) = &-\frac{Ze^2}{r} + \int e^2\frac{[\rho(\mathbf{r}')-\sigma(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}dr' \\ &+ v_{xc}[\rho(\mathbf{r})] - \nu\Theta(R-r) \ .\end{aligned} \tag{24}$$

But now $\sigma(\mathbf{r})$ contains a small nonspherical part and, in consequence, so does $\rho(\mathbf{r})$. Just as σ was separated into terms independent of x, linear in x, and quadratic in x, so the same is done with $\rho(\mathbf{r})$ and $v(\mathbf{r})$. This permits us to do the same for the orbital functions and the one-electron energies:

$$\psi_i(\mathbf{r}) = \psi^0_i(\mathbf{r}) + x\psi^1_i(\mathbf{r}) + x^2\psi^2_i(\mathbf{r}) + \cdots \ , \tag{25}$$

$$\varepsilon_i = \varepsilon^0_i + x\varepsilon^1_i + x^2\varepsilon^2_i + \cdots \ . \tag{26}$$

The one-electron equations then can be separated into a series of perturbation equations,

$$(h^0-\varepsilon^0_i)\psi^0_i = 0 \ , \tag{27}$$

$$(h^0-\varepsilon^0_i)\psi^1_i = (\varepsilon^1_i - v^1)\psi^0_i \ , \tag{28}$$

and so on. It turns out that ψ^2_i is not needed so we can stop at this point. In the above h^0 is the same as h in Eq. (24) except that

$$v^0(\mathbf{r})=-\frac{Ze^2}{r}+\int e^2\frac{[\rho^0(\mathbf{r}')-\sigma^0(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+v_{xc}(\rho^0)-\nu\Theta(R-r) \tag{29}$$

is substituted for $v(\mathbf{r})$. In the first-order equation above

$$v^1(\mathbf{r})=\int e^2\frac{[\rho^1(\mathbf{r}')-\sigma^1(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'+\rho^1(\mathbf{r})\frac{\partial v_{xc}}{\partial\rho^0} . \tag{30}$$

The relation between ρ and the orbital functions is, as before,

$$\begin{aligned}\rho(\mathbf{r})&=\sum_{n_i}|\psi_i(\mathbf{r})|^2\\&=\sum_{n_i}|\psi_i^0+x\psi_i^1\cdots|^2\\&=\sum_{n_i}|\psi_i^0(\mathbf{r})|^2+x\sum_{n_i}[\psi_i^{0*}(\mathbf{r})\psi_i^1(\mathbf{r})+\text{c.c.}]+\cdots\\&=\rho^0(\mathbf{r})+x\rho^1(\mathbf{r})+\cdots .\end{aligned} \tag{31}$$

$\rho^0(\mathbf{r})$ and $v^0(\mathbf{r})$ are spherically symmetric and are the charge density of the unperturbed atom in jellium. $\rho^1(\mathbf{r})$ and $v^1(\mathbf{r})$ have the same $\cos\Theta$ angular behavior as σ^1. They require the solutions, $\psi_i^1(\mathbf{r})$, of the first-order perturbation equations. This is accomplished by an iterative Green-function technique described in Ref. 13–15.

In addition to the above, we need an expression for the change in energy. An easy way to get the required expression is through the Feynman-Hellman theorem. It has been verified by Slater that the Feynman-Hellman theorem applies to self-consistent field models, but we will repeat the proof here in the context of our atom-in-jellium model. The energy functional E depends on the displacement x both through σ and the orbital functions ψ_i. Thus the derivative of E with respect to x is

$$\frac{dE}{dx}=\int\frac{\delta E}{\delta\sigma}\frac{d\sigma}{dx}d\mathbf{r}+\sum_i\int\left[\frac{\delta E}{\delta\psi_i^*}\frac{\delta\psi_i^*}{\delta x}+\frac{\sigma E}{\sigma\psi_i}\frac{\delta\psi_i}{\delta x}\right]d\mathbf{r} . \tag{32}$$

The Feynman-Hellman theorem depends on showing that the second term on the right is zero. Since $\delta J/\delta\psi_i^*=0$ one has

$$\frac{\delta E}{\delta\psi_i^*}=[\varepsilon_i+\nu\Theta(R-r)]\psi_i . \tag{33}$$

Thus the second term is

$$\begin{aligned}&\sum_i\int[\varepsilon_i+\nu\Theta(R-r)]\left[\psi_i\frac{\delta\psi_i^*}{\delta x}+\psi_i^*\frac{\delta\psi_i}{\delta x}\right]d\mathbf{r}\\&\quad=\sum_i\varepsilon_i\frac{d}{dx}\int|\psi_i(\mathbf{r})|^2d\mathbf{r}+\frac{d}{dx}\int\nu\Theta(R-r)\rho(\mathbf{r})d\mathbf{r} .\end{aligned} \tag{34}$$

Because the normalization integrals of the orbital functions are constants independent of x and the charge neutrality constraint is also independent of x, these terms are all zero.

This leaves

$$\begin{aligned}\frac{dE}{dx}&=\int\frac{\delta E}{\delta\sigma}\frac{d\sigma}{dx}d\mathbf{r}\\&=\frac{d\sigma}{dx}\left[\frac{Ze^2}{r}-\int e^2\frac{[\rho(\mathbf{r}')-\sigma(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\right]d\mathbf{r} .\end{aligned} \tag{35}$$

This is the Feynman-Hellman theorem for our case. We want a perturbation expansion of this result. On the left of this expression we have

$$E=E_0+xE_1+x^2E_2+\cdots \tag{36}$$

and

$$\frac{dE}{dx}=E_1+2xE_2+\cdots ; \tag{37}$$

and on the right side we have

$$\frac{d\sigma}{dx}=\sigma^1+2x\sigma^2+\cdots \tag{38}$$

and

$$\begin{aligned}v_c(\mathbf{r})&=-\frac{Ze^2}{r}+\int e^2\frac{[\rho(\mathbf{r}')-\sigma(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\\&=v_c^0+xv_c^1+\cdots .\end{aligned} \tag{39}$$

v_c^0 is the spherically symmetric part of the Coulomb potential,

$$v_c^0(r)=-\frac{Ze^2}{r}+\int e^2\frac{[\rho^0(\mathbf{r}')-\sigma^0(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' , \tag{40}$$

and $v_c^1(\mathbf{r})$ is the part deriving from $\sigma^1(\mathbf{r})$ and $\rho^1(\mathbf{r})$:

$$v_c^1(\mathbf{r})=\int e^2\frac{[\rho^1(\mathbf{r}')-\sigma^1(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' . \tag{41}$$

Using these definitions we find

$$E_1=\int\sigma^1(\mathbf{r})v_c^0(\mathbf{r})d\mathbf{r} \tag{42}$$

and

$$2E_2=-\int[\sigma^1(\mathbf{r})v_c^1(\mathbf{r})+2\sigma^2(\mathbf{r})v_c^0(\mathbf{r})]d\mathbf{r} . \tag{43}$$

Because $\sigma^1(r)$ and $\sigma^2(r)$ vanish except at $r=R$ and because $v_c^0(r)$ and $dv_c^0(r)/dr$ are both zero at $r=R$, E_1 is zero and E_2 reduces to

$$E_2=-\tfrac{1}{2}\int\sigma^1(\mathbf{r})v_c^1(\mathbf{r})d\mathbf{r} . \tag{44}$$

We thus have the change in energy associated with small displacements. It requires the solution of only the first-order perturbation equations. This fortunate circumstance is seen to depend on having built electrical neutrality into our model.

In order to obtain equation of state information about condensed matter from our single atom-in-jellium model it was necessary to introduce a somewhat arbitrary separation of the energy into a part associated with the atom and a part belonging with the jellium. This was made easier through the introduction of a muffin-tin form for the charge density in the jellium outside of the atomic sphere.

We face a similar problem in the case of the perturbed atom-in-jellium model. After some experimentation we have fixed on a similar solution: The perturbed charge density, $\rho^1(\mathbf{r})$, is replaced by its volume average outside the atomic sphere. Since $\rho^1(\mathbf{r})$ is proportional to $\cos\Theta$, its average in the outer region is just zero. A further result is that the perturbation to the potential, $v^1(\mathbf{r})$, is also zero outside the atomic sphere. This simplifies the solution of the equations for $\psi_i^1(\mathbf{r})$.

The arguments for applying the muffin-tin average to $\rho^1(\mathbf{r})$ are the following: (1) it very much simplifies the computational problems when one can avoid using numerical methods in the outer region; and (2) the behavior of $\rho^1(\mathbf{r})$, $v^1(\mathbf{r})$, and $\psi_i^1(\mathbf{r})$ in the outer region will not resemble what happens in real condensed matter where the outer region contains other atoms and not a jellium.

We have completed the description of our atom-in-jellium model of atomic vibrations. In the following section we will apply it to a variety of elemental solids and will calculate Debye temperatures and Grüneisen constants.

IV. COMPARISON OF CALCULATIONS AND EXPERIMENTAL DATA

Is the Einstein oscillator model capable of giving useful estimates of heat capacities associated with lattice vibrations? Our aim in developing this model is to use it in the calculation of equations of state of highly compressed matter where detailed measurements are impossible and a theoretical model is needed. We believe self-consistent field electronic structure models become better at high densities, but we are forced to confront our model with experimental data obtained at normal density since high density data is not available.

Before proceeding with a comparison of our calculations and data based on experiments, a word should be said about other theoretical models. There are two we want to mention. The first is the extension of the electronic structure calculations developed here to distortions of a crystal lattice by phonons. This has been done in a few cases using the pseudopotential method with the expected excellent results.[16,17] A second approach is to relate sound velocities in a crystal to the bulk modulus and then use the Debye model to predict the Debye temperature and Grüneisen constant. Moruzzi and Janak[18] use this approach and their very good band-structure calculations of bulk moduli to determine the vibrational properties of 14 simple metals.

Our model directly calculates an Einstein oscillator frequency, ν_E (actually an energy proportional to ν_E^2). This implies a delta function density of states which will replace the actual density of phonon states. A comparison of this frequency with moments of the true density of states provides a basis of comparison. Fortunately a compendium of these moments and other related data is available.[19] Use of the second moment seems best for two reasons: as stated above that is the quantity we actually calculate; and the second moment is directly connected with the deviation of the heat capacity from the Dulong and Petite high-temperature limit. Table I give a comparison of the *ab initio* Einstein model with the data given by Landolt-Börnstein.[19] All elements where either moments or high-temperature Debye temperatures are listed in Ref. 19 are included in our table with the exception of three lanthanides, where our self-consistent field program has convergence problems, and three elements (As, Sb, and Bi) which do not have close-packed structures. All the data we have taken from Ref. 19 are based on fitting Born–von Karman models to phonon data from neutron scattering. In addition we include two elements (Ti and Zr) for which careful analyses of the high-temperatures calorimetric data are available.[20]

The differences between our calculations and the experiment-based Debye temperatures are, on average, about 15 percent of the Debye temperature. We regard this as satisfactory for a single frequency model. Doing better will require more realistic phonon densities of states which means going beyond the atom-in-jellium model.

In Fig. 2, Debye temperatures for the 3*d*, 4*d*, and 5*d* transition metals and some other elements in the same

TABLE I. Root-mean-square phonon frequencies, Debye temperatures (high-T limit) and calculated Debye temperatures for thirty-three close-packed elements. Data from Ref. 19 except for Ti and Zr which come from Ref. 20.

		Second moment		High T	Calculated
Element	Z	ν_2 (THz)	Θ_D (K)	Θ_D (K)	Θ_D (K)
Li	3	8.31	399	397	491
Na	11	3.47	167		192
Mg	12	6.67	320	320	393
Al	13	8.48	407	405	535
K	19	2.13	102	100	127
Ca	20			220	250
Sc	21			316	368
Ti	22	7.32	351		440
V	23	7.22	347		486
Cr	24	9.55	458		482
Fe	26	8.77	421	418	349
Co	27			375	338
Ni	28	8.01	384	384	335
Cu	29	6.60	317	318	314
Zn	30			240	260
Rb	37	1.33	64	63	79
Sr	38			~150	161
Y	39			209	253
Zr	40	5.32	255		315
Nb	41	5.84	280	285	364
Mo	42	7.79	374	370	371
Ru	44			404	321
Pd	46	6.02	289		227
Ag	47	4.45	214	215	195
Cd	48			170	165
In	49			136	142
Hf	72			200	235
Ta	73	4.71	226		277
W	74	6.40	307	310	289
Pt	78	4.94	237		193
Au	79	3.85	185	183	155
Pb	82	1.95	94		79
Th	90	2.99	144	143	209

rows of the periodic table are shown. It would be interesting if one could correlate the trends shown in Fig. 2 with some feature in the electronic structure (e.g., volume per atom or number of d electrons per atom), but we have not been able to do so.

All of the calculated Debye temperatures in Table I and Fig. 2 were computed with atomic sphere radii corresponding to normal density metals. Calculations at other densities lead to a Debye temperature as a function of molar volume, $\Theta_D(V)$. Of particular interest is the Grüneisen coefficient,

$$\gamma=\frac{V}{C_V}\left[\frac{\partial P}{\partial T}\right]_V , \tag{45}$$

which in the Debye and Einstein models is

$$\gamma=-\frac{\partial \log\Theta_D}{\partial \log V}=-\frac{\partial \log\Theta_E}{\partial \log V} . \tag{46}$$

The thermodynamic definition of the Grüneisen parameter [Eq. (45)] is equal to

$$\gamma=\alpha_V B_T V/C_V , \tag{47}$$

where α_V is the volumetric thermal expansion coefficient, B_T is the isothermal bulk modulus, and C_V is the constant volume heat capacity. These are all measurable quantities and therefore a comparison is possible between Eq. (47) (measured γ) and Eq. (46) (calculated γ). Equation (46) should really be augmented by an electronic excitation term. At room temperature electronic excitation correction is fairly small and will be neglected here, but we note that the atom-in-jellium model can be used to compute it.

In Fig. 3 we present our calculations of the lattice

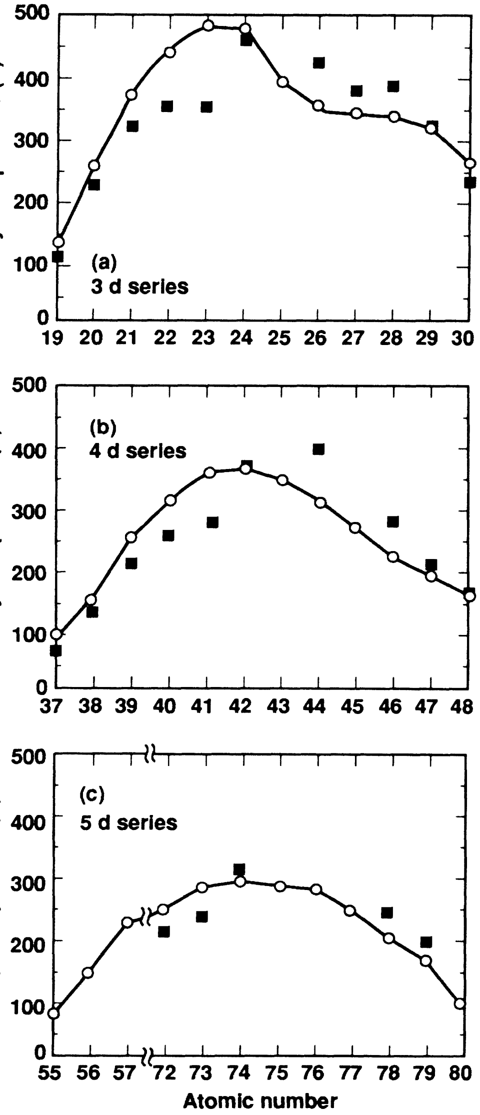

FIG. 2. Transition metal Debye temperatures as calculated by the atom-in-jellium model (○) and derived from experimental data (■) (Refs. 19 and 20).

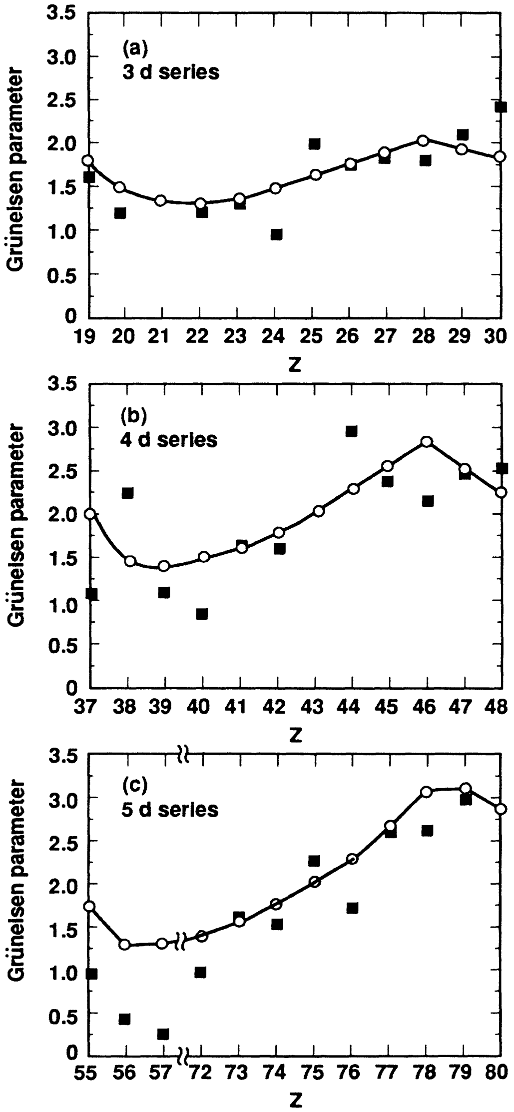

FIG. 3. Transition metal Grüneisen coefficients as calculated by the atom-in-jellium model (○) and derived from thermodynamic data (■) (Ref. 21).

Grüneisen constants and experimental ones based on data tabulated in a compilation by Smithells.[21] Agreement is poorer than in the case of Debye temperatures. Possibly some of the disagreement is due to the difficulty of making good measurements; some is probably due to anharmonic effects in lattice vibrations at room temperatures; the remainder of the discrepancy must be related to the shortcomings of a single atom model. In making comparison of experimental and calculated Debye temperatures, it was possible to avoid the problem of anharmonic effects by using phonon data based on neutron scattering. For the Grüneisen parameter we are forced to use thermodynamic data that includes anharmonic effects, contributions from imperfections and impurities in crystals, and electronic excitations.

ACKNOWLEDGMENTS

We wish to acknowledge a helpful discussion with Dr. Duane Wallace whose book (Ref. 20) contained some of the data in Table I and who informed us of the reference for the rest of the data in Table I. This work was done at the Los Alamos National Laboratory and Lawrence Livermore National Laboratory for the U.S. Department of Energy under Contract Nos. W-7405-ENG-36 and W-7405-ENG-48.

APPENDIX

Atom-in-jellium models require both bound and continuum orbital functions. The bound-state orbital functions are few in number and present no problems that are not found in atomic self-consistent-field calculations. Continuum functions are less familiar and obvious pitfalls exist such as resonances where the amplitude of an orbital function changes rapidly in a small energy interval. To deal with this problem, Wigner's R-matrix method[22] has been modified and adapted to our needs.

The problem is this: We have a one-electron Hamiltonian with a short-range potential (spherically symmetric everywhere and zero or constant outside the atomic sphere),

$$H\phi_E = E\phi_E \ . \tag{A1}$$

We want to find the continuum functions ϕ_E in terms of a discrete set of basis functions,

$$\phi_E = \sum_i C_i(E)\phi_i \ . \tag{A2}$$

where the basis functions are determined numerically by solving the Hamiltonian equation at the basis function energies,

$$H\phi_i = E_i\phi_i \ . \tag{A3}$$

Wigner's method requires that the ϕ_i's satisfy a boundary condition at the atomic sphere radius and thereby specifies a complete orthogonal discrete set of functions in terms of which ϕ_E can be expanded. The problem with this is that in general no single basis function ϕ_i closely resembles the required continuum function ϕ_E and therefore a large number of basis functions will be required for good accuracy. Instead we have chosen to use smaller energy intervals between our basis functions and to deal with the resulting nonorthogonality.

As a practical matter we have found that *two* basis functions are sufficient for an energy interval of a few volts. Three energy intervals and four equally spaced basis functions will yield very good accuracy at normal solid densities. In the next paragraphs an interpolation scheme is outlined for regular solutions of the Schrödinger equation; the case of the Dirac equation (used in our calculations) is only slightly different.

Positive-energy solutions ϕ_i of the Schrödinger equation at energies E_i are obtained numerically to form our basis. The overlap matrix

$$I_{ij} = \int_0^R \phi_i^* \phi_j \, d\mathbf{r} \tag{A4}$$

is needed. The expansion of Eq. (A2) leads to

$$I_{iE} = \int_0^R \phi_i^* \phi_E \, d\mathbf{r} = \sum_j I_{ij} C_j(E) \ , \tag{A5}$$

which can be solved,

$$C_j(E) = \sum_i (I^{-1})_{ji} I_{iE} \ , \tag{A6}$$

when the quantities I_{iE} have been obtained. A reference function ϕ_0 at energy $E_0 \neq E_i$, must also be obtained as a numerical solution of the Schrödinger equation and also through an expansion in terms of the basis functions:

$$\phi_0^* = \sum_i C_i^* \phi_i^* \ . \tag{A7}$$

Its overlap integrals with the basis functions are

$$I_{0j} = \int_0^R \phi_0^* \phi_j \, d\mathbf{r} = \sum_i C_i^* I_{ij} \ , \tag{A8}$$

which can be inverted to give

$$C_i^* = \sum_j I_{0j} (I^{-1})_{ji} \ . \tag{A9}$$

Next Green's theorem is used to give

$$W_{iE} = \int_0^R [(H\phi_i)^* \phi_E - \phi_i^* (H\phi_E)] d\mathbf{r} = (E_i - E) I_{iE} \tag{A10}$$

$$= -\tfrac{1}{2} \int \left[\frac{\partial \phi_i^*}{\partial r} \phi_E - \phi_i^* \frac{\partial \phi_E}{\partial r} \right]_{r=R} ds \tag{A11}$$

and thus W_{iE} and hence I_{iE} will be known when ϕ_E and $\partial\phi_E/\partial r$ are known at $r = R$. Green's theorem may also be applied to ϕ_0 and ϕ_E, and, with the use of Eq. (A7), the overlap integral I_{0E} becomes

$$\begin{aligned} I_{0E} &= \int_0^R \phi_0^* \phi_E \, d\mathbf{r} = \frac{W_{0E}}{E_0 - E} \\ &= \sum_i C_i^* \int_0^R \phi_i^* \phi_E \, d\mathbf{r} = \sum_i C_i^* \frac{W_{iE}}{E_i - E} \ . \end{aligned} \tag{A12}$$

The relation

$$\frac{W_{0E}}{E_0 - E} = \sum_i C_i^* \frac{W_{iE}}{E_i - E} \tag{A13}$$

can be solved for the logarithmic derivative

$$L_E = \frac{\partial \phi_E(R)}{\partial R} \Big/ \phi_E(R) = N_E / D_e \ , \tag{A14}$$

where

$$N_E = \sum_i C_i^* \frac{\partial \phi_i^*}{\partial R} \Big/ (E_i - E) - \frac{\partial \phi_0^*}{\partial R} \Big/ (E_0 - E) \tag{A15a}$$

and

$$D_E = \sum_i C_i^* \phi_i(R)/(E_i - E) - \phi_0^*(R)/(E_i - E) \ . \tag{A15b}$$

The normalization of ϕ_E is given by its large r behavior:

$$\phi_E(r) = [j_l(kr)\cos\delta(E) - n_l(kr)\sin\delta(E)]Y_{lm}(\Omega), \quad r \geq R \ . \tag{A16}$$

Now Eqs. (A6), (A10), (A11), (A14), and (A16) contain all the relations necessary to evaluate the expansion coefficients $C_i(E)$. The development given above has been implemented in a computer program which uses the Dirac equation rather than the Schrödinger equation.

The approximation scheme for regular continuum functions will now be tested by using it to calculate the phase shift $\delta(E)$ and the partial density of states,

$$I_{EE} = \int_0^R \phi_E^* \phi_E d\mathbf{r} \ , \tag{A17}$$

in the $3d_{3/2}$ channel for normal density copper ($R = 2.67a_0$). Outside the atomic sphere there is a constant exchange-correlation potential, $v_\infty = -0.3191$ hartrees; the Fermi energy is at $E_F = +0.0326$ hartrees; and the four basis functions are at $E_i = -0.3191$, -0.1913, -0.0634, and $+0.0645$ hartrees. In each energy interval we use the two basis functions at the interval end points, and one of the basis functions outside the interval serves as a reference function. Results for the energy interval containing resonance are shown in Figs. 4(a) and 4(b). The phase shift shown in Fig. 4(b) is that obtained by numerically integrating the Dirac equation at 50 energies in that interval and the error is the difference between phase shifts computed by the modified R-matrix method and numerical ones. The error is clearly very small. In Fig. 4(a), the partial density of states is displayed. Again the error is very small. It is worth emphasizing that the basis functions are both well away from the resonance.

Our next task is to develop a similar scheme for interpolating the irregular solutions of the Schrödinger equation which are needed in the construction of the Green function. Our development is based on integrals which are bilinear in the regular and irregular functions. The first nine equations of the preceding section are repeated with no other change:

$$H\psi_E = E\psi_E \ , \tag{A1'}$$

$$\psi_E = \sum_i d_i(E)\psi_i \ , \tag{A2'}$$

$$H\psi_i = E_i\psi_i \ , \tag{A3'}$$

$$J_{ij} = \int_0^R \phi_i^* \psi_j d\mathbf{r} \ , \tag{A4'}$$

$$J_{iE} = \int_0^R \phi_i^* \psi_E d\mathbf{r} = \sum_j J_{ij} d_j(E) \ , \tag{A5'}$$

$$d_j(E) = \sum_j (J^{-1})_{ji} J_{iE} \ , \tag{A6'}$$

$$\phi_0^* = \sum_i \mathcal{C}_i^* \phi_i^* \ , \tag{A7'}$$

$$J_{0j} = \int_0^R \phi_0^* \psi_j d\mathbf{r} = \sum_i \mathcal{C}_i^* J_{ij} \ , \tag{A8'}$$

$$\mathcal{C}_i^* = \sum_j J_{0j} (J^{-1})_{ji} \ . \tag{A9'}$$

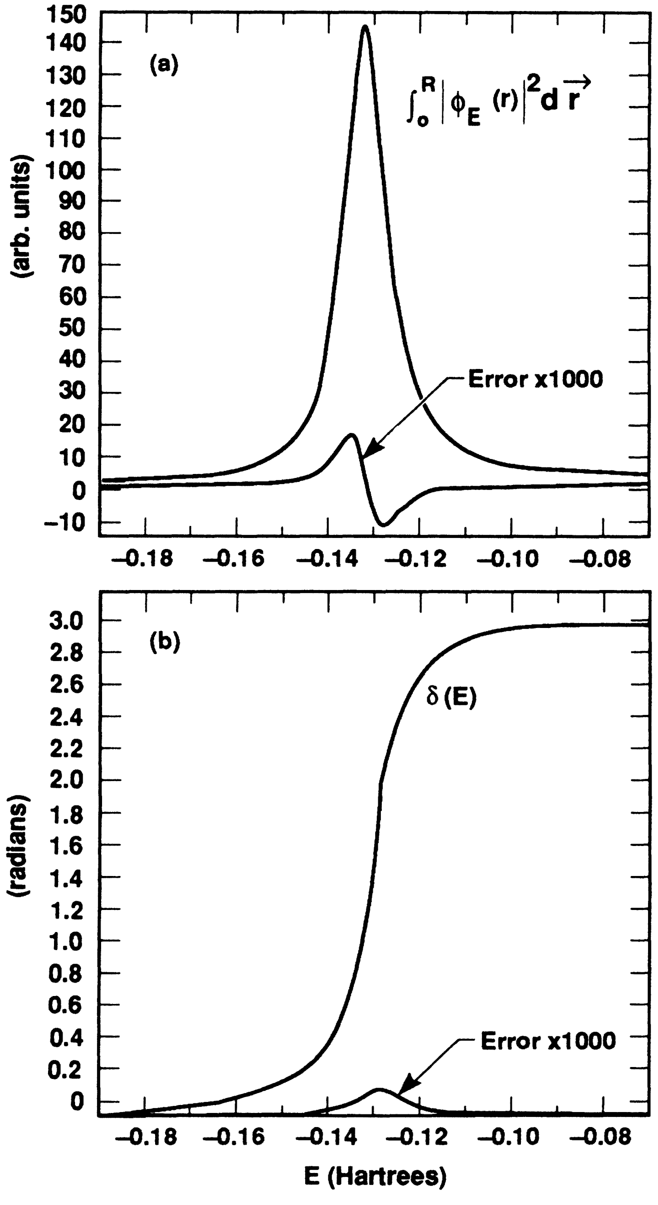

FIG. 4. (a) Partial density of states and (b) phase shift for copper in the $3d_{3/2}$ channel near the $3d$ resonance.

The overlap matrix J_{ij}, unlike I_{ij}, is not symmetric. It is worth noting that J_{ij} and I_{ij}, as used in our calculations, are ill-conditioned matrices, and some care is needed in determining the matrix elements. The basic energies E_i, the basic functions ϕ_i, and the reference functions ϕ_0 are the same as for the expansion of ϕ_E; the expansion coefficients of ϕ_0^* are, however, different though only slightly so.

The analogs of Eqs. (A10) and (A11) are

$$X_{iE}=\int_0^R[(H\phi_i)^*\psi_E-\phi_i^*(H\psi_E)]d\mathbf{r}=(E_i-E)J_{iE} \tag{A10$'$}$$

$$\begin{aligned}&=-\tfrac{1}{2}\int\left[\frac{\partial\phi_i^*}{\partial r}\psi_E-\phi_i^*\frac{\partial\psi_E}{\partial r}\right]_{r=R}dS\\&\quad+\tfrac{1}{2}\int\left[\frac{\partial\phi_i^*}{\partial r}\psi_E-\phi_i\frac{\partial\psi_E}{\partial r}\right]_{r=0}dS\\&=X_{iE}^R-X_{iE}^0\ ,\end{aligned} \tag{A11$'$}$$

where

$$J_{iE}=\frac{X_{iE}}{E_i-E}=\frac{X_{iE}^R-X_{iE}^0}{E_i-E}\ .$$

We require the large r form of ψ_E to be

$$\psi_E(\mathbf{r})=[j_l(kr)\sin\delta(E)+n_l(kr)\cos\delta(E)]Y_{lm}(\Omega),\quad r\geq R \tag{A16$'$}$$

so that the Green function, $G_E(r,r')$, constructed from ϕ_E and ψ_E has the proper outgoing-wave boundary conditions. [The phase shift $\delta(E)$ in Eq. (A16′) is the same as that in Eq. (A16)]. With Eq. (A16′) and the known values of ϕ_i and $\partial\phi_i/\partial r$ at $\mathbf{r}=R$, X_{iE}^R is obtained directly.

To determine X_{iE}^0 we examine the overlap integral involving the reference function and ψ_E:

$$\begin{aligned}J_{0E}&=\int_0^R\phi_0^*\psi_E d\mathbf{r}=\frac{X_{0E}}{E_0-E}\\&=\sum_i\mathcal{C}_i^*\int_0^R\phi_i\psi_E d\mathbf{r}=\sum_i\mathcal{C}_i^*\frac{X_{iE}}{E_i-E}\ .\end{aligned} \tag{A12$'$}$$

This equation may be rewritten in the form

$$\frac{X_{0E}^0}{E_0-E}-\sum_i\mathcal{C}_i^*\frac{X_{iE}^0}{E_0-E}=\frac{X_{0E}^R}{E_0-E}-\sum_i\mathcal{C}_i^*\frac{X_{iE}^R}{E_i-E}\ . \tag{A13$'$}$$

The right side,

$$\sigma(E)=\frac{X_{0E}^R}{E_0-E}-\sum_i\mathcal{C}_i^*\frac{X_{iE}^R}{E_i-E}\ , \tag{A17$'$}$$

contains known boundary values of ϕ_0, ϕ_i, and ψ_E only. The left side of (A13′) depends, in part, on the values of ϕ_0 and ϕ_i near $r=0$. We may choose them to be

$$\begin{aligned}&\phi_i(\mathbf{r})=\phi_0(\mathbf{r})=r^lY_{lm}(\mathbf{r})\ ,\\&\frac{\partial\phi_i(\mathbf{r})}{\partial\mathbf{r}}=\frac{\partial\phi_0(\mathbf{r})}{\partial\mathbf{r}}=lr^{l-1}Y_{lm}(\Omega),\quad r\rightarrow0\ .\end{aligned} \tag{A18}$$

This results in

$$X_{iE}^0=X_{0E}^0 \tag{A19}$$

and hence

$$\begin{aligned}\frac{X_{0E}}{E_0-E}-\sum_i\mathcal{C}_i^*\frac{X_{iE}^0}{E_i-E}&=X_{0E}^0\left[\frac{1}{E_0-E}-\sum\mathcal{C}_i^*\frac{1}{E_i-E}\right]\\&=X_{0E}^0\tau(E)\ .\end{aligned} \tag{A20}$$

Now the preceding equations give us definite values for X_{iE}^0 and X_{iE}^R, so the expansion coefficients $d_i(E)$ can be determined using Eqs. (A6′) and (A13′).

A test of the interpolated irregular function will complete this development. In analogy to the case of regular functions we examine

$$J_{EE}=\int_0^R\phi_E^*\psi_E d\mathbf{r} \tag{A21}$$

using both numerical solutions of the Dirac equation and interpolated functions. Again we look at the $3d_{3/2}$ resonance as we suspect this energy region will be the most difficult to handle. The numerical values of J_{EE} and the errors,

$$J_{EE}\ (\text{interpolated})-J_{EE}\ (\text{numerical})\ . \tag{A22}$$

are shown in Fig. 5. The errors are an order of magnitude larger than in the case of the regular functions but still are quite small.

The interpolation scheme outlined in this appendix is rather different from usual interpolation methods and has its pitfalls as well as its advantages. The main advantages are accuracy and the ability to deal with resonances. The main pitfalls seem to be associated with the fact that the matrices I_{ij} and J_{ij} are ill-conditioned. If the basis function energies E_i are too close together these matrices become more ill-conditioned and trouble will result. A way out of this difficulty may be to use a single basis function rather than two as in all of our calculations. This has not

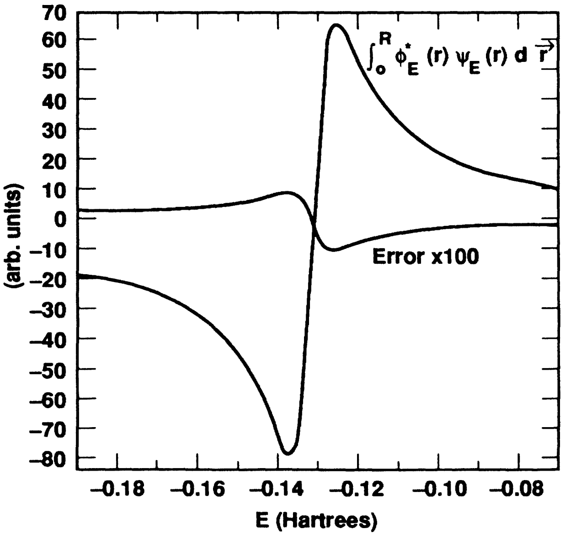

FIG. 5. Overlap integral for regular and irregular functions in the $3d_{3/2}$ channel near the copper $3d$ resonance,

been tried. We have found that using Green's theorem to evaluate the off-diagonal elements of I_{ij} and J_{ij} is a bad practice; the off-diagonal elements should be evaluated by the same numerical integration methods used for the diagonal elements. This will give better accuracy to the off-diagonal elements and probably also results in a cancellation of errors when the inverses of I_{ij} and J_{ij} are computed.

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