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Electron-phonon interaction and the ground state of metallic hydrogen

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Time-independent perturbation theory has been developed for a many-body system of electrons and nuclei, where the unperturbed states are formed from the product of oscillator functions and Slater determinants of plane waves. The theory is applied to metallic hydrogen. The expansion is simplified by isolating certain subseries which correspond to the energy levels of known simpler systems, and the remaining terms are computed through second order. The perturbed energy levels are given in terms of two parameters: the Wigner-Seitz parameter r_s and the ratio m/M of the electron to the nuclear mass. Anharmonicity relative to harmonic terms depends upon $(m/r_sM)^{1/2}$. An expansion for the energy difference between two states is obtained by subtracting the leading terms of a pair of perturbation expansions. A condition is proposed which indicates when the normal state is the ground state of the system. The normal state has a particularly simple parameter expansion. A numerical series for this state has been computed, and it is found that the lattice dynamics has a large influence on the binding energy.

I. INTRODUCTION

The electron-phonon interaction in metals was studied initially by Fröhlich,[1] Bardeen and Pines,[2] and other authors noted in these references. A summary of more recent work based on Green's functions may be found elsewhere.[3,4] For the most part, studies have been concerned with approximations for the complex behavior of a typical metal. The only metal that, at present, offers the possibility of being treated precisely is metallic hydrogen, which is the case considered here. To carry out this study a perturbation theory is developed for computing the stationary energy levels of a many-body system of electrons and nuclei. For reasons discussed in Sec. III field-theoretic methods are avoided in favor of a computation in many-body configuration space. The object is not to develop accurate approximate solutions for the energy, since these already exist, but to look for a systematic expansion with exact expressions for the leading terms. Assume that two states of interest have such an expansion. Then the leading terms in the energy difference are also exact, and the expansion should be useful for examining the slight energy difference between a normal and a superconducting state. The calculation becomes practical because a large part of the leading terms is the same for both states.

The perturbation theory is developed in the high-density limit of metallic hydrogen, and the question arises as to whether the result can be continued into the region of principal interest near the equilibrium density. This question is examined in Sec. VI, where the energy of a normal state is computed for comparison with the results of other methods. In Sec. II the electron-phonon interaction is defined, and in Secs. III—VII the perturbation approach is described and carried out. The electron-phonon energy is discussed in more detail in Sec. VIII. In Sec. IX the conditions under which the normal state is the ground state of the system are investigated, and the results are summarized in Sec. X.

II. DEFINITION OF THE ELECTRON-PHONON INTERACTION

In a complex metal it is not entirely obvious how a general electron-phonon interaction should be defined, but for metallic hydrogen the problem is simpler. The electron-nuclei interaction is

$$H^{e\text{-}n} = -e^2 \sum_i \sum_j \frac{1}{|\mathbf{r}_i - \mathbf{R}_j|}, \tag{1}$$

where $-e$ is the electronic charge, $\mathbf{r}_i$ gives the position of the ith electron, and $\mathbf{R}_j$ gives the position of the jth nucleus. The difference between this interaction and that for a given lattice is called the general electron-phonon interaction (more properly, the electron-lattice-displacement interaction):

$$H^{e\text{-ph}} = -e^2 \sum_i \sum_j \left[\frac{1}{|\mathbf{r}_i - \mathbf{R}_j|} - \frac{1}{|\mathbf{r}_i - \mathbf{R}_{0j}|} \right], \tag{2}$$

where $\mathbf{R}_{0j}$ is a fixed lattice point. The phonons to be considered here are bare phonons from oscillations in a uniform background charge, consistent with the use of free-electron wave functions. Thus, dispersion curves of the type that are normally measured do not apply, since the measured curves apply for phonons which carry electronic screening charge. In fact, the use of free electrons and screened phonons as a basis for evaluating the energy would lead to additional divergence problems.

III. OUTLINE OF THE MANY-BODY PERTURBATION THEORY

A. Choice of perturbation theory

Although many-body theory in the form of Green's functions is commonly used to discuss the ground state of a system, such theory is most useful for excited-state approximations and thermal properties. The ground-state computation is a more exacting problem. The approach used here is that of ordinary Rayleigh-Schrödinger perturbation theory in n-dimensional configuration space. One important difference between these approaches is the following: the former attempts to give the ground state, itself, as determined by particle interactions, while the perturbation theory attempts only to follow the many-body energy levels. Thus a discontinuous change in dynamical ground-state symmetry with the strength of some perturbation introduces no problems, for it simply corresponds to the crossover of continuous energy levels whose symmetries are essentially unchanged. The energy levels followed are the stationary states of the system, as opposed to one-particle approximations that decay with time which appear in Green's-function theory.

The limitations of the present approach follow (1) from the fact that, in principle, the ground state is obtained only after a comparison of all relevant energy levels, and (2) problems with degeneracy and convergence must be dealt with.

B. Description of the approach

Expansions are made in terms of Slater determinants of plane waves for the electrons and harmonic-oscillator functions for the nuclei. Each many-body energy level arises from a different unperturbed state. The level which arises from the unperturbed function described by a Fermi sphere of occupied vectors in wave-vector space will be referred to as the spherical normal state, or simply the normal state. In reality, this level is not quite the normal ground state for a crystal lattice, since the unperturbed ground-state wave function should be taken to have the symmetry demanded of the perturbed function, and a Fermi sphere applies only for an electron gas. However, in metallic hydrogen where the Fermi surface does not touch the first Brillouin-zone boundary, the difference between the results obtained for a spherical Fermi surface and, for example, results obtained for a slightly distorted Fermi surface with cubic symmetry, is not expected to be of critical importance.[5] The possibility remains for more dramatic distortions to be of interest as a result of electron-phonon interactions.

In principle, it might be expected that degenerate perturbation theory should be used for all states except that described by the Fermi sphere, since all other unperturbed states are degenerate. However, this will not be done, and the following assumptions will be made: In large many-body systems degeneracy can be ignored as long as the nondegenerate theory does not lead to a spurious divergence. It is also assumed that no special problems arise at level crossings.[6]

The mechanics of evaluating the perturbation series may be summarized as follows. The complete series is broken up into appropriate subseries. Some of the subseries, such as that involving only electron-electron interactions, must be taken to all orders, whereas others require only low orders. The subseries are taken to represent simpler systems which have already been computed. The complete result for a given crystal lattice and a given unperturbed state is an expansion in terms of two parameters: the Wigner-Seitz parameter r_s and the ratio m/M of electronic to nuclear mass. However, these parameters are not the independent parameters. Since the ratio of harmonic to anharmonic terms in the lattice vibration is found to depend upon fractional powers of m/r_sM, it is useful to treat r_s and m/r_sM as the independent parameters.

IV. ENERGY CALCULATION

A. The Hamiltonian

Consider the Hamiltonian

$$H=T^e+T^n+\tfrac{1}{2}\sum_j\sum_{i\,(\neq j)}\frac{e^2}{r_{ij}}-\sum_i\sum_j\frac{e^2}{|\mathbf{r}_i-\mathbf{R}_j|}+\tfrac{1}{2}\sum_j\sum_{i\,(\neq j)}\frac{e^2}{R_{ij}}\,, \tag{3}$$

where T^e and T^n are the kinetic-energy operators for the electrons and nuclei. Terms for a fixed lattice and uniform background charge can be added and subtracted in (3); and since, to good approximation, electrons in a metal move through a periodic potential, it is convenient to introduce this potential explicitly. Let V^p denote the periodic potential energy due to a fixed lattice of charges neutralized by a uniform negative background:

$$V^p=\sum_i\left[\frac{e^2N}{V}\int\frac{d\mathbf{r}}{|\mathbf{r}_i-\mathbf{r}|}-\sum_j\frac{e^2}{|\mathbf{r}_i-\mathbf{R}_{0j}|}\right], \tag{4}$$

where N is the number of electrons, or nuclei, and V is the volume of the system. The Hamiltonian for N noninteracting electrons moving in the periodic potential is

$$H^p=T^e+V^p\,. \tag{5}$$

Let H^l denote the Hamiltonian of a lattice of N nuclei vibrating in the uniform background charge:

$$H^l=T^n+\frac{e^2}{2}\sum_j\sum_{i\,(\neq j)}\left[\frac{1}{\mathbf{R}_{ij}}-\frac{1}{\mathbf{R}_{0ij}}\right]-\frac{e^2N}{V}\sum_j\int d\mathbf{r}\left[\frac{1}{|\mathbf{r}-\mathbf{R}_j|}-\frac{1}{|\mathbf{r}-\mathbf{R}_{0j}|}\right], \tag{6}$$

where terms for a fixed lattice have been subtracted. If (5) and (6) are substituted into (3), one obtains

$$H=H^p+H^l+H^{e\text{-}e}+H^{e\text{-ph}}+H^{\text{back}}+V_0\,, \tag{7}$$

where

$$H^{e\text{-}e}=\tfrac{1}{2}\sum_j\sum_{i\,(\neq j)}\frac{e^2}{r_{ij}} \tag{8}$$

is the electron-electron interaction, and

$$H^{\text{back}}=-\frac{e^2N}{V}\sum_i\int\frac{d\mathbf{r}}{|\mathbf{r}_i-\mathbf{r}|}+\frac{e^2N}{V}\sum_j\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}_j|}-\frac{e^2}{2}\frac{N^2}{V^2}\int\frac{d\mathbf{r}\,d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \tag{9}$$

includes terms left over due to the introduction of the background charge. V_0 is a constant representing the electrostatic energy of a fixed lattice in a uniform background given by

$$V_0=\frac{e^2}{2}\left[\frac{N}{V}\right]^2\int\frac{d\mathbf{r}\,d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}-\frac{e^2N}{V}\sum_j\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}_{0j}|}+\frac{e^2}{2}\sum_j\sum_{i\,(\neq j)}\frac{1}{R_{0ij}}\ . \tag{10}$$

Consider finally the harmonic approximation H^{hl} for the lattice Hamiltonian H^l, and let

$$H=H_0+H'+V_0\ , \tag{11}$$

where H_0 is the unperturbed Hamiltonian,

$$H_0=T^e+H^{hl}\ , \tag{12}$$

and

$$H'=H^{e\text{-}e}+H^{e\text{-ph}}+V^p+H^l-H^{hl}+H^{\text{back}} \tag{13}$$

is the perturbation.

B. Perturbation series

The unperturbed wave functions ψ_ν and eigenvalues ε_ν, where ν denotes the double subscript $k\kappa$, are given by

$$\psi_\nu=\psi_k\psi_\kappa\ , \tag{14}$$

$$\varepsilon_\nu=\varepsilon_k+\varepsilon_\kappa \tag{15}$$

obtained from the equations

$$T^e\psi_k=\varepsilon_k\psi_k\ , \tag{16}$$

$$H^{hl}\psi_\kappa=\varepsilon_\kappa\psi_\kappa\ . \tag{17}$$

ψ_k is a determinant of N one-electron plane waves of the form

$$\psi_{kj}=\frac{1}{\sqrt{V}}e^{i\mathbf{k}_j\cdot\mathbf{r}}\xi_j\ , \tag{18}$$

where ξ_j is the spin function and k denotes a set of wave vectors $\mathbf{k}_1,\dots,\mathbf{k}_N$ with a spin index implied. ψ_κ is a product of oscillator functions, where κ denotes a set of phonon wave vectors with a polarization index included, giving $3N$ oscillator functions.[7] The principal difference between the bare phonons described by these functions and screened phonons is in the mode which is nearly longitudinal, where the frequency of the former does not approach zero, but approaches a plasma frequency for long wavelengths.

The many-body energy levels, labeled by the unperturbed states, are given by

$$E_\nu=V_0+\varepsilon_\nu+H'_{\nu\nu}+\sum_{\nu'\neq\nu}\frac{H'_{\nu\nu'}H'_{\nu'\nu}}{\varepsilon_\nu-\varepsilon_{\nu'}}+\cdots\ , \tag{19}$$

carried to all orders. This series may be manipulated by recognizing various subseries which are known. If all terms in H' are set equal to zero except V^p, one obtains, apart from the constant, the series

$$E'_\nu=\varepsilon_\kappa+\varepsilon_k+V^p_{kk}+\sum_{k'\neq k}\frac{V^p_{kk'}V^p_{k'k}}{\varepsilon_k-\varepsilon_{k'}}+\cdots\ , \tag{20}$$

since V^p depends only on electronic terms, and the oscillator functions integrate to unity. However, this expansion gives an energy level for the Hamiltonian

$$H=H_0+V^p=H^p+H^{hl}\ , \tag{21}$$

and $E'_\nu-\varepsilon_\kappa$ is an eigenvalue E^p_k for the Hamiltonian H^p. E^p_k can be computed either from the many-body perturbation series (20), or from one-electron energy-band theory.[8]

In a similar way, by setting all terms in H' equal to zero except H^l-H^{hl}, one obtains the rapidly converging series

$$E''_\nu=\varepsilon_k+\varepsilon_\kappa+(H^l-H^{hl})_{\kappa\kappa}+\sum_{\kappa'\neq\kappa}\frac{(H^l-H^{hl})_{\kappa\kappa'}(H^l-H^{hl})_{\kappa'\kappa}}{\varepsilon_\kappa-\varepsilon_{\kappa'}}+\cdots\ , \tag{22}$$

and $E''_\nu-\varepsilon_k$ is just an eigenvalue E^l_κ for the Hamiltonian H^l defined by (6). Finally, the series

$$E^c_k=\sum_{k'\neq k}\frac{H^{e\text{-}e}_{kk'}H^{e\text{-}e}_{k'k}}{\varepsilon_k-\varepsilon_{k'}}+\cdots \tag{23}$$

represents the correlation energy of an interacting electron gas,[9] which, for a normal-state wave function, has already been computed to an appreciable number of terms.[10] The series (23) has no meaning except as a summation to all orders, since the second-order term is ill behaved, but problems of this nature are restricted to the electron-electron interaction. The remaining terms in (19) are well behaved in second order. Since the physical nature of the problem ensures that an energy function exists, it follows that if divergence occurs in higher orders, in principle, one can form additional subseries to give finite results. When the series given by (20), (22), and (23) are isolated in (19), one obtains

$$E_\nu=V_0+E^p_k+E^c_k+E^l_\kappa+H^{\text{int}}_{\nu\nu}+\sum_{\nu'\neq\nu}\frac{1}{\varepsilon_\nu-\varepsilon_{\nu'}}[H^{\text{int}}_{\nu\nu'}H^{\text{int}}_{\nu'\nu}-H^{e\text{-}e}_{\nu\nu'}H^{e\text{-}e}_{\nu'\nu}+H^{\text{int}}_{\nu\nu'}(V^p+H^l-H^{hl})_{\nu'\nu}+(V^p+H^l-H^{hl})_{\nu\nu'}H^{\text{int}}_{\nu'\nu}]+\cdots\ , \tag{24}$$

where, for convenience, a new interaction term,

$$H^{\text{int}}=H^{e\text{-}e}+H^{e\text{-ph}}+H^{\text{back}}\ , \tag{25}$$

has been defined. H^{int} is the interaction for the subsystems H^p and H^l, since it is equal to $H-H^p-H^l-V_0$.

In the expression given by (24), terms of the type $V^p_{\nu\nu'}(H^l-H^{hl})_{\nu'\nu}$ do not appear because if $\kappa'\neq\kappa$ the electronic term in the product will vanish, and if $k'\neq k$ the phonon term will vanish. The expansion (24) has the form of an expansion where $E^p_k+E^c_k+E^l_\kappa$ is the zerothorder term, but where all succeeding terms are evaluated with the simple wave functions for H_0.

C. Matrix elements and energy expressions

For a sum of one-electron potential terms $H(i)$ in the Hamiltonian, the diagonal elements for k space are

$$\left[\sum_i H(i)\right]_{kk}=\frac{N}{V}\int H(1)d\mathbf{r}_1\,, \tag{26}$$

and, for the two-particle interaction,

$$H_{kk}^{e\text{-}e}=\frac{e^2}{2}\frac{N(N-1)}{V^2}\int\frac{d\mathbf{r}_1 d\mathbf{r}_2}{r_{12}}+E_k^{\text{ex}}\,, \tag{27}$$

where

$$E_k^{\text{ex}}=\frac{-e^2}{2V^2}\sum_j\sum_{i\,(\neq j)}\langle\xi_i\,|\,\xi_j\rangle\int\frac{e^{i(\mathbf{k}_j-\mathbf{k}_i)\cdot\mathbf{r}_{12}}}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2 \tag{28}$$

is the exchange energy. The matrix elements needed in (24) are

$$H_{\nu\nu'}^{\text{int}}=H_{kk'}^{e\text{-}e}\delta_{\kappa\kappa'}+H_{\nu\nu'}^{e\text{-ph}}+H_{\nu\nu'}^{\text{back}}\,, \tag{29}$$

$$V_{\nu\nu'}^{p}=V_{kk'}^{p}\delta_{\kappa\kappa'}\,, \tag{30}$$

and

$$(H^l-H^{hl})_{\nu\nu'}=(H^l-H^{hl})_{\kappa\kappa'}\delta_{kk'}\,. \tag{31}$$

Owing to cancellations from the background terms, one obtains from the above expressions

$$H_{\nu\nu}^{\text{int}}=E_k^{\text{ex}}+\frac{e^2N}{V}\sum_j\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}_{0j}|}-\frac{e^2N}{V^2}(N+\tfrac{1}{2})\int\frac{d\mathbf{r}\,d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\,, \tag{32}$$

and as the volume $V\rightarrow\infty$ this expression becomes just

$$H_{\nu\nu}^{\text{int}}=E_k^{\text{ex}}-V_{kk}^{p}\,. \tag{33}$$

The off-diagonal terms are as follows: if only phonons and no electrons are excited, the matrix elements of V^p and $H^{e\text{-}e}$ obviously vanish, and a calculation shows the same to be true for H^{int}. For a double excitation of electrons, only the terms $H_{\nu\nu'}^{e\text{-}e}H_{\nu'\nu}^{e\text{-}e}$ are involved in second order, and these terms cancel in (24). Since for excitations higher than two all matrix elements vanish, only intermediate states with singly excited electrons are of interest. For a single excitation where the one-electron state ψ_{k_l} in the set k is replaced by $\psi_{k_{l'}}$ to form the set k', the matrix elements are

$$\left[\sum_i H(i)\right]_{kk'}=\langle\xi_l\,|\,\xi_{l'}\rangle\frac{1}{V}\int e^{i(\mathbf{k}_{l'}-\mathbf{k}_l)\cdot\mathbf{r}_1}H(1)d\mathbf{r}_1 \tag{34}$$

and

$$H_{kk'}^{e\text{-}e}=\frac{e^2}{V^2}(N-1)\langle\xi_l\,|\,\xi_{l'}\rangle\int\frac{e^{i(\mathbf{k}_{l'}-\mathbf{k}_l)\cdot\mathbf{r}_2}}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2-\frac{e^2}{V^2}\langle\xi_l\,|\,\xi_{l'}\rangle\sum_{i\,(\neq l)}\langle\xi_l\,|\,\xi_i\rangle\int\frac{e^{i(\mathbf{k}_{l'}-\mathbf{k}_i)\cdot\mathbf{r}_1}e^{i(\mathbf{k}_i-\mathbf{k}_l)\cdot\mathbf{r}_2}}{r_{12}}d\mathbf{r}_1\,d\mathbf{r}_2\,. \tag{35}$$

The corresponding matrix element for H^{back} is given by $-N/(N-1)$ times the first integral on the right-hand side of Eq. (35), but both integrals in (35) are nonvanishing only because the system is bounded. Thus, if surface effects are ignored, $H_{kk'}^{e\text{-}e}$ and $H_{kk'}^{\text{back}}$ vanish, and

$$H_{kk'}^{\text{int}}=H_{kk'}^{e\text{-ph}} \tag{36}$$

for a single excitation.

It follows from these results that

$$E_\nu=V_0+E_k^p-V_{kk}^p+E_k^{\text{ex}}+E_k^c+E_\kappa^l+\sum_{\kappa'}\sum_{\substack{k'\\ \text{single ex.}}}\frac{|H_{k\kappa,k'\kappa'}^{e\text{-ph}}|^2}{\varepsilon_k-\varepsilon_{k'}+\varepsilon_\kappa-\varepsilon_{\kappa'}}+\sum_{\substack{k'\\ \text{single ex.}}}\frac{H_{k\kappa,k'\kappa}^{e\text{-ph}}V_{k'k}^p+\text{c.c.}}{\varepsilon_k-\varepsilon_{k'}}+\cdots\,, \tag{37}$$

where the ellipsis corresponds to third- and higher-order terms. It may be anticipated that the two terms in second order are related to screening of nuclei by the electrons. The matrix elements are given by

$$H_{k\kappa,k'\kappa'}^{e\text{-ph}}=-\frac{e^2}{V}\langle\xi_l\,|\,\xi_{l'}\rangle\int e^{i(\mathbf{k}_{l'}-\mathbf{k}_l)\cdot\mathbf{r}_1}\sum_j\left[\frac{1}{|\mathbf{r}_1-\mathbf{R}_j|}-\frac{1}{|\mathbf{r}_1-\mathbf{R}_{0j}|}\right]_{\kappa\kappa'}d\mathbf{r}_1 \tag{38}$$

and

$$V_{kk'}^p=\frac{e^2}{V}\langle\xi_l\,|\,\xi_{l'}\rangle\int e^{i(\mathbf{k}_{l'}-\mathbf{k}_l)\cdot\mathbf{r}_1}\left[\frac{N}{V}\int\frac{d\mathbf{r}}{|\mathbf{r}_1-\mathbf{r}|}-\sum_j\frac{1}{|\mathbf{r}_1-\mathbf{R}_{0j}|}\right]d\mathbf{r}_1\,. \tag{39}$$

To evaluate the electron-phonon interaction let the terms in large parentheses in (38) be written as a Fourier integral:

$$\left[\frac{1}{|\mathbf{r}_1-\mathbf{R}_j|}-\frac{1}{|\mathbf{r}_1-\mathbf{R}_{0j}|}\right]_{\kappa\kappa'}$$

$$=\frac{1}{2\pi^2}\int\frac{d\mathbf{k}\,e^{i\mathbf{k}\cdot\mathbf{r}_1}}{k^2}e^{-i\mathbf{k}\cdot\mathbf{R}_{0j}}(e^{-i\mathbf{k}\cdot\mathbf{u}_j}-1)_{\kappa\kappa'}\,, \tag{40}$$

where $\mathbf{u}_j=\mathbf{R}_j-\mathbf{R}_{0j}$. In substituting this expression into (38), one encounters the integral

$$\int_V e^{i\mathbf{q}\cdot\mathbf{r}_1}d\mathbf{r}_1\rightarrow(2\pi)^3\delta(\mathbf{q}) \tag{41}$$

as $V\rightarrow\infty$, where $\mathbf{q}=\mathbf{k}_{l'}-\mathbf{k}_l+\mathbf{k}$. Thus, with surface effects again ignored, it follows that, for a single excitation where $\mathbf{k}_l$ goes to $\mathbf{k}_{l'}$,

$$H^{e\text{-ph}}_{k\kappa,k'\kappa'}=-\frac{4\pi e^2}{V}\frac{\langle\xi_l\,|\,\xi_{l'}\rangle}{|\mathbf{k}_{l'}-\mathbf{k}_l|^2}$$

$$\times\sum_j e^{i(\mathbf{k}_{l'}-\mathbf{k}_l)\cdot\mathbf{R}_{0j}}(e^{i(\mathbf{k}_{l'}-\mathbf{k}_l)\cdot\mathbf{u}_j}-1)_{\kappa\kappa'}\,. \tag{42}$$

In a similar way, one obtains

$$V^p_{kk'}=-\frac{4\pi e^2}{V}\frac{\langle\xi_l\,|\,\xi_{l'}\rangle}{|\mathbf{k}_{l'}-\mathbf{k}_l|^2}\sum_j e^{i(\mathbf{k}_{l'}-\mathbf{k}_l)\cdot\mathbf{R}_{0j}}$$

$$=-\frac{4\pi e^2N}{V}\langle\xi_l\,|\,\xi_{l'}\rangle\sum_{\mathbf{K}}\frac{\delta_{\mathbf{k}_{l'}-\mathbf{k}_l,\mathbf{K}}}{K^2}\,, \tag{43}$$

where $\mathbf{K}$ is a reciprocal-lattice vector.

V. EVALUATION OF THE SECOND-ORDER ENERGY FOR SMALL VALUES OF m/r_sM

A. The electron-phonon term

For equal numbers of plus and minus spins, the second-order terms in (37) are

$$E^{(2)}_\nu=2\sum_{\kappa'}\sum_l\sum_{l'}\frac{|H^{e\text{-ph}}_{k\kappa,k'\kappa'}|^2}{\varepsilon_k-\varepsilon_{k'}+\varepsilon_\kappa-\varepsilon_{\kappa'}}+4\sum_l\sum_{l'}\frac{H^{e\text{-ph}}_{k\kappa,k'\kappa}V^p_{k'k}}{\varepsilon_k-\varepsilon_{k'}}\,, \tag{44}$$

where the dependence of the matrix elements on l and l' is obtained from (42) and (43), and the sum over spin has been performed. The sums over l and l' are, respectively, over occupied and unoccupied wave vectors with plus spin. The first term in (44) will be called the electron-phonon term, and the second the mixed term.

For a single electronic excitation, $\varepsilon_{k'}-\varepsilon_k$ is equal to $\hbar^2(k_{l'}^2-k_l^2)/2m$, which in rydberg units (1 Ry$=e^2/2a_B$, with a_B the Bohr radius) is

$$\varepsilon_{k'}-\varepsilon_k=a_B^2(k_{l'}^2-k_l^2)=\left[\frac{9\pi}{4}\right]^{2/3}\frac{1}{r_s^2}\frac{k_{l'}^2-k_l^2}{k_F^2}\,, \tag{45}$$

where $k_F=(9\pi/4)^{1/3}(r_sa_B)^{-1}$ is the radius of the Fermi sphere, and $4\pi(r_sa_B)^3/3=V/N$. If κ represents the state of zero-point motion and κ' represents a state where the oscillator with wave vector $\boldsymbol{\kappa}$ and polarization labeled by s is excited to the first quantum level,

$$\varepsilon_{\kappa'}-\varepsilon_\kappa=\hbar\omega(\boldsymbol{\kappa}s)=\frac{2\sqrt{3}}{r_s^{3/2}}\left[\frac{m}{M}\right]^{1/2}\frac{\omega(\boldsymbol{\kappa}s)}{\omega(01)}\,, \tag{46}$$

with the last expression given in rydbergs. ω is the phonon frequency, and $\omega(01)$ is the $\boldsymbol{\kappa}=\mathbf{0}$ longitudinal frequency (plasma frequency). The fact that $\omega(01)$ reduces to a plasma frequency rather than zero is crucial for the convergence of the second-order energy expression. The matrix elements for parallel spins given by (42) can be expanded in the series

$$H^{e\text{-ph}}_{k\kappa,k'\kappa'}=-\frac{4\pi e^2}{V}\frac{1}{|\mathbf{k}_{l'}-\mathbf{k}_l|^2}\sum_j e^{i(\mathbf{k}_{l'}-\mathbf{k}_l)\cdot\mathbf{R}_{0j}}\{i(\mathbf{k}_{l'}-\mathbf{k}_l)\cdot(\mathbf{u}_j)_{\kappa\kappa'}-\tfrac{1}{2}[(\mathbf{k}_{l'}-\mathbf{k}_l)\cdot\mathbf{u}_j]^2_{\kappa\kappa'}+\cdots\}\,, \tag{47}$$

where each power of $\mathbf{k}\cdot\mathbf{u}_j$ introduces a factor $(r_sM)^{-1/4}$ and the nonvanishing matrix elements $(\mathbf{u}_j)_{\kappa\kappa'}$ relative to the zero-point motion are those for a single phonon. To lowest order in the parameter m/r_sM, the electron-phonon term in (44) is determined by the first term in the expansion (47), and the mixed term in (44) is determined by the second term in (47) with $\kappa'=\kappa$. Higher powers in $\mathbf{u}_j$ in this expansion may be viewed in the same sense as anharmonicities. The leading contribution to the electron-phonon term in rydbergs (with $\hbar\omega$ also measured in rydbergs) is

$$E^{(2)e\text{-ph}}_\nu=-2N\frac{m}{M}\left[\frac{8\pi a_B^3}{V}\right]^2\sum_s\sum_{\substack{l\\ \text{occ.}}}\sum_{\substack{l'\\ \text{unocc.}}}\frac{\left|\dfrac{\mathbf{k}_{l'}-\mathbf{k}_l}{|\mathbf{k}_{l'}-\mathbf{k}_l|}\cdot\mathbf{v}(\boldsymbol{\kappa}s)\right|^2}{\hbar\omega(\boldsymbol{\kappa}s)a_B^2\,|\mathbf{k}_{l'}-\mathbf{k}_l|^2[a_B^2(k_{l'}^2-k_l^2)+\hbar\omega(\boldsymbol{\kappa}s)]}\,, \tag{48}$$

where $\mathbf{v}$ is the polarization vector,

$$\boldsymbol{\kappa}=\mathbf{k}_{l'}-\mathbf{k}_l-\mathbf{K} \tag{49}$$

and $\mathbf{K}$ is the reciprocal-lattice vector which for each value of $\mathbf{k}_{l'}-\mathbf{k}_l$ puts $\boldsymbol{\kappa}$ in the first Brillouin zone. If the sums are changed to integrals, (48) becomes, with the aid of (45) and (46),

$$E_\nu^{(2)e\text{-ph}} = -\frac{N}{\sqrt{3}\pi^4}\left[\frac{9\pi}{4}\right]^{2/3}\frac{1}{r_s}\left[\frac{r_s m}{M}\right]^{1/2} \times \sum_s \int d\mathbf{p}\, n(\mathbf{p}) \int \frac{d\mathbf{p}'[1-n(\mathbf{p}')]\left|\frac{\mathbf{p}'-\mathbf{p}}{|\mathbf{p}'-\mathbf{p}|}\cdot\mathbf{v}(\boldsymbol{\kappa}s)\right|^2}{\frac{\omega(\boldsymbol{\kappa}s)}{\omega(01)}|\mathbf{p}'-\mathbf{p}|^2\left[p'^2-p^2+2\sqrt{3}\left[\frac{4}{9\pi}\right]^{2/3}\left[\frac{r_s m}{M}\right]^{1/2}\frac{\omega(\boldsymbol{\kappa}s)}{\omega(01)}\right]}, \tag{50}$$

where $\mathbf{p}=\mathbf{k}/k_F$, and $\boldsymbol{\kappa}$ is now given by

$$\boldsymbol{\kappa}=k_F(\mathbf{p}'-\mathbf{p})-\mathbf{K}\ . \tag{51}$$

$n(\mathbf{p})$ is the average occupation number for plus (or minus) spin near a point in p space. For the normal state described by a Fermi sphere, the integration is restricted to $p<1$ and $p'>1$.

B. The mixed term

To lowest order in m/r_sM, with $\hbar\omega$ and the right-hand result again in rydbergs,

$$4\sum_l\sum_{l'}\frac{H^{e\text{-ph}}_{k\kappa,k'\kappa}V^p_{k'k}}{\varepsilon_k-\varepsilon_{k'}} = \frac{128\pi^2 a_B^2 N}{V^2}\frac{m}{M}\sum_l\sum_{l'}\sum_\kappa\sum_s\sum_{\mathbf{K}\neq 0}\frac{\left|\frac{\mathbf{K}}{|\mathbf{K}|}\cdot\mathbf{v}(\boldsymbol{\kappa}s)\right|^2\delta_{\mathbf{k}_{l'}-\mathbf{k}_l,\mathbf{K}}}{K^2\hbar\omega(\boldsymbol{\kappa},s)(k_{l'}^2-k_l^2)}$$

$$= \frac{2a_B^2 N}{\pi^4}\frac{m}{M}\sum_s\sum_{\mathbf{K}\neq 0}\frac{1}{K^2}\int\frac{d\boldsymbol{\kappa}}{\hbar\omega(\boldsymbol{\kappa},s)}\left|\frac{\mathbf{K}}{|\mathbf{K}|}\cdot\mathbf{v}(\boldsymbol{\kappa},s)\right|^2\int\frac{d\mathbf{k}\,n(\mathbf{k})}{K^2+2\mathbf{K}\cdot\mathbf{k}}, \tag{52}$$

where the integral over $\boldsymbol{\kappa}$ covers the first Brillouin zone, and it has been assumed that the occupied region is such that $\mathbf{k}_l+\mathbf{K}$ is an unoccupied state. The appearance of the reciprocal-lattice vectors $\mathbf{K}$ may be traced to the fact that the periodic potential V^p changes the electronic charge density from a uniform distribution into a distribution with lattice symmetry. The latter may be written as $\sum_{\mathbf{K}} a(\mathbf{K})e^{i\mathbf{K}\cdot\mathbf{r}}$, where, except for a numerical coefficient, $a(\mathbf{K})$ is given by the factor[11]

$$\frac{k_F}{K^2}\int\frac{d\mathbf{k}\,n(\mathbf{k})}{K^2+2\mathbf{K}\cdot\mathbf{k}} = \frac{\pi}{2}\frac{k_F^2}{K^2}\left\{1+\frac{k_F}{K}\left[1-\left[\frac{K}{2k_F}\right]^2\right]\ln\left[\frac{K/2k_F+1}{K/2k_F-1}\right]\right\} \tag{53}$$

for the case of the normal state. Substitution of (53) into (52) leads to

$$4\sum_l\sum_{l'}\frac{H^{e\text{-ph}}_{k\kappa,k'\kappa}V^p_{k'k}}{\varepsilon_k-\varepsilon_{k'}} = \frac{\sqrt{3}}{\pi}\left[\frac{4}{9\pi}\right]^{1/3}N\left[\frac{m}{r_sM}\right]^{1/2}\sum_s\sum_{K\neq 0}\frac{k_F^2}{K^2}\left\{1+\frac{k_F}{K}\left[1-\left[\frac{K}{2k_F}\right]^2\right]\ln\left[\frac{K+2k_F}{K-2k_F}\right]\right\}\left\langle\frac{\omega(01)}{\omega(\boldsymbol{\kappa}s)}\left|\frac{\mathbf{K}}{|\mathbf{K}|}\cdot\mathbf{v}(\boldsymbol{\kappa}s)\right|^2\right\rangle, \tag{54}$$

where the angular brackets indicate an average over $\boldsymbol{\kappa}$. If the average is approximated by separate averages for the two factors, one obtains the value $2.6N(m/r_sM)^{1/2}$ for the right-hand side of (54) in the case of the normal state.

VI. ENERGY OF THE NORMAL STATE FOR A bcc LATTICE

A. Expansion for zeroth- and first-order terms

For notational purposes let the series (37) be written as a perturbation expansion

$$E_\nu=E_\nu^{(0)}+E_\nu^{(1)}+E_\nu^{(2)}+E_\nu^{(3)}+\cdots\ , \tag{55}$$

where the superscript denotes the order, and the first two terms are defined as

$$E_\nu^{(0)}+E_\nu^{(1)}=V_0+E_k^p-V_{kk}^p+E_k^{\text{ex}}+E_k^c+E_\kappa^l\ . \tag{56}$$

As calculated by the perturbation expansion (20) for the spherical normal state of a bcc lattice, E_k^p is given in rydberg units by[5]

$$E_k^p - V_{kk}^p = N[2.21/r_s^2 - 0.0905 - 0.018 r_s + O(r_s^2)] \tag{57}$$

in a numerical approximation. The electron-gas correlation energy E^c has the expansion[10]

$$E_k^c = N[\,0.0622 \ln r_s - 0.096 + 0.018 r_s \ln r_s - 0.036 r_s + O(r_s^2, r_s^2 \ln r_s)] \tag{58}$$

(the coefficient of the term in r_s is only a rough approximation), and the free-electron exchange energy is

$$E_k^{\text{ex}} = -\frac{0.916N}{r_s}\ . \tag{59}$$

Finally, for a body-centered-cubic lattice, V_0 is equal to $-1.792N/r_s$, and[12]

$$E_\kappa^l = N\left\{\frac{2.65}{r_s^{3/2}}\left[\frac{m}{M}\right]^{1/2} + \frac{0.73}{r_s^2}\left[\frac{m}{M}\right] + O\left[\left[\frac{m}{M}\right]^{3/2} r_s^{-5/2}\right]\right\}. \tag{60}$$

Combining these results, one obtains

$$E_\nu^{(0)} + E_\nu^{(1)} = N\left\{\frac{2.21}{r_s^2} - \frac{2.708}{r_s} - 0.187 + 0.0622 \ln r_s - 0.054 r_s + 0.018 r_s \ln r_s + O(r_s^2, r_s^2 \ln r_s) + \frac{2.65}{r_s}\left[\frac{m}{r_s M}\right]^{1/2} + \frac{0.73}{r_s}\left[\frac{m}{r_s M}\right] + O\left[\frac{1}{r_s}\left[\frac{m}{r_s M}\right]^{3/2}\right]\right\}. \tag{61}$$

The expansion is observed to be a double series with the first involving ascending powers of r_s, along with ascending powers of r_s multiplied by $\ln r_s$; this series represents the energy for a fixed lattice. The second series gives the harmonic and anharmonic energies of the lattice vibrations, and is in the form of an ascending series in $(m/r_s M)^{1/2}$ multiplied by r_s^{-1}. It must be assumed that m/M is always a smaller parameter than r_s.

The value of $E_\nu^{(2)}$, estimated in the Appendix, added to the result of Eq. (61), is plotted in Fig. 1. The good agreement with other calculations, of which Wigner's calculation is shown, for the case of the fixed lattice terms, indicates that the perturbation expansion is still quite good in the neighborhood of the equilibrium density.

VII. THIRD- AND HIGHER-ORDER PERTURBATIONS

The third-order terms in (19) are given by

$$\sum_{\mu\neq\nu}\sum_{\lambda\neq\nu}\frac{H'_{\nu\mu}H'_{\mu\lambda}H'_{\lambda\nu}}{(\varepsilon_\nu-\varepsilon_\mu)(\varepsilon_\nu-\varepsilon_\lambda)} - H'_{\nu\nu}\sum_{\mu\neq\nu}\frac{H'_{\nu\mu}H'_{\mu\nu}}{(\varepsilon_\nu-\varepsilon_\mu)^2}\ , \tag{62}$$

and therefore the third-order terms in (24) are

$$\begin{aligned} E_\nu^{(3)} = {} & \sum_{\mu\neq\nu}\sum_{\lambda\neq\nu}\frac{1}{(\varepsilon_\nu-\varepsilon_\mu)(\varepsilon_\nu-\varepsilon_\lambda)}[H'_{\nu\mu}H'_{\mu\lambda}H'_{\lambda\nu} - V^p_{\nu\mu}V^p_{\mu\lambda}V^p_{\lambda\nu} - (H^l-H^{hl})_{\nu\mu}(H^l-H^{hl})_{\mu\lambda}(H^l-H^{hl})_{\lambda\nu} - H^{e\text{-}e}_{\nu\mu}H^{e\text{-}e}_{\mu\lambda}H^{e\text{-}e}_{\lambda\nu}] \\ & - \sum_{\mu\neq\nu}\frac{1}{(\varepsilon_\nu-\varepsilon_\mu)^2}[H'_{\nu\nu}H'_{\nu\mu}H'_{\mu\nu} - V^p_{\nu\nu}V^p_{\nu\mu}V^p_{\mu\nu} - (H^l-H^{hl})_{\nu\nu}(H^l-H^{hl})_{\nu\mu}(H^l-H^{hl})_{\mu\nu} - H^{e\text{-}e}_{\nu\nu}H^{e\text{-}e}_{\nu\mu}H^{e\text{-}e}_{\mu\nu}]\ , \end{aligned} \tag{63}$$

where terms in the first series with $\mu=\lambda$ may be combined with the second series. The terms may be separated into those which apply for a fixed lattice and those which result from the nuclear displacement. The first group of terms has been evaluated previously[5] for the case of a bcc lattice in the normal state, giving the small result

$$E^{(3)}_{\text{fixed lattice}} \approx 0.001 r_s N\ , \tag{64}$$

in rydbergs. Most of the terms for the nuclear displacements involve combinations of matrix elements of $H^l - H^{hl}$, V^p, and $H^{e\text{-ph}}$, and these terms tend to introduce higher powers of $m/r_s M$. An example of a term which is not of this type is the term

$$\sum_{k'\neq k}\sum_{\kappa'\neq\kappa}\frac{(H^{e\text{-}e}_{k'k'} - H^{e\text{-}e}_{kk})}{(\varepsilon_k - \varepsilon_{k'} + \varepsilon_\kappa - \varepsilon_{\kappa'})^2} H^{e\text{-ph}}_{k\kappa,k'\kappa'} H^{e\text{-ph}}_{k'\kappa',k\kappa}\ .$$

Evaluation of this expression is obtained by simply introducing the factor

$$\frac{E^{\text{ex}}_{k'} - E^{\text{ex}}_k}{\varepsilon_{k'} - \varepsilon_k + \varepsilon_{\kappa'} - \varepsilon_\kappa} = \frac{1}{\pi^2}\left[\frac{4}{9\pi}\right]^{1/3} r_s \frac{\int d\mathbf{p}''\left[\dfrac{1}{|\mathbf{p}''-\mathbf{p}|^2} - \dfrac{1}{|\mathbf{p}''-\mathbf{p}'|^2}\right] n(\mathbf{p}'')}{p'^2 - p^2 + 2\sqrt{3}\left[\dfrac{4}{9\pi}\right]^{2/3}\left[\dfrac{r_s m}{M}\right]^{1/2}\dfrac{\omega(\boldsymbol{\kappa} s)}{\omega(01)}} \tag{65}$$

into the integrand in Eq. (50). Thus, the result is of order $r_s E^{(2)e\text{-ph}}$, and if all terms in third order were well behaved one could conclude immediately that $E^{(3)}$ is the order of r_s times $E^{(2)}$, after the neglect of various small terms in m/r_sM. Unfortunately, at least one term in third order, arising from the expression

$$\sum_{\substack{k'\neq k \\ k'\neq k''}} \sum_{k''\neq k} \sum_{\kappa'\neq\kappa} \frac{H^{e\text{-ph}}_{k\kappa,k'\kappa'} H^{e\text{-}e}_{k'\kappa',k''\kappa'} H^{e\text{-ph}}_{k''\kappa',k\kappa}}{(\varepsilon_k-\varepsilon_{k'}+\varepsilon_\kappa-\varepsilon_{\kappa'})(\varepsilon_k-\varepsilon_{k''}+\varepsilon_\kappa-\varepsilon_{\kappa'})} ,$$

leads to divergent integrals, but since the energy must be finite, it may be assumed that divergence from individual terms is removed when the series is summed to all orders. It is postulated that the principal effect of such summation is simply to introduce $\ln r_s$ terms into the basic r_s dependence. Without further investigation it will be assumed that $\sum_{n=3}^{\infty} E_\nu^{(n)}$ corresponds to higher orders in r_s and m/r_sM than $E_\nu^{(2)}$, in the sense that the ratio of the two can be made arbitrarily small by a choice of small values for r_s and m/M.

VIII. ELECTRON-PHONON ENERGY FOR AN ARBITRARY STATE

Consider the second-order electron-phonon energy written in the form

$$E_\nu^{(2)e\text{-ph}} = -\frac{N}{\sqrt{3}\pi^4}\left[\frac{9\pi}{4}\right]^{2/3}\frac{1}{r_s}\left[\frac{r_sm}{M}\right]^{1/2} \times\sum_s \int d\mathbf{p}\, n(\mathbf{p}) \int d\mathbf{p}'[1-n(\mathbf{p}')]F(\mathbf{p},\mathbf{p}',s) , \tag{66}$$

where for small m/r_sM, $F(\mathbf{p},\mathbf{p}',s)$ is defined by Eq. (50). $F(\mathbf{p},\mathbf{p}',s)$ depends on the parameter $(r_sm/M)^{1/2} = r_s(m/r_sM)^{1/2}$ in its denominator. If p_2 denotes the maximum value of p for which $n(\mathbf{p})$ is nonvanishing, and p_1 is the minimum value for which $1-n(\mathbf{p})$ is nonvanishing,

$$\int d\mathbf{p}\, n(\mathbf{p}) \int d\mathbf{p}'[1-n(\mathbf{p}')]F(\mathbf{p},\mathbf{p}',s) = \int_0^{p_2} dp \int_{p_1}^{\infty} dp' \int d\Omega_p \int d\Omega_{p'} p^2 p'^2 n(\mathbf{p})[1-n(\mathbf{p}')]F(\mathbf{p},\mathbf{p}',s) , \tag{67}$$

where $d\Omega_p$ is the angular part of the differential. Then,

$$\int_0^{p_2} dp \int_{p_1}^{\infty} dp' = \int_0^{p_1} dp \int_{p_1}^{\infty} dp' + \int_{p_1}^{p_2} dp \int_{p_2}^{\infty} dp' + \int_{p_1}^{p_2} dp \int_{p_1}^{p_2} dp' . \tag{68}$$

The first two terms on the right-hand side involve different domains for $\mathbf{p}$ and $\mathbf{p}'$, where $p'>p$, while in the third term the domains overlap. For the normal state $p_1=p_2=1$ and this term vanishes. Consider the special case where p_2 and p_1 differ from unity by a very small amount, such that, for the longitudinal-type mode, p_2-p_1 is small compared with $2\sqrt{3}(4/9\pi)^{2/3}(r_sm/M)^{1/2}\omega(\kappa s)/\omega(01)$. In this case p'^2-p^2 can be neglected in the denominator for $F(\mathbf{p},\mathbf{p}',s)$, and one obtains a small Coulomb-like term proportional to $1/r_s$ in expression (66). It may be concluded that the largest part of $E^{(2)}$ is proportional to $(m/r_sM)^{1/2}$, but for states very close to the normal state, one finds, in addition, an approximate $1/r_s$ dependence (independent of mass in the limit). The latter is very small but it can be quite important in the energy difference between two states.

IX. ENERGY DIFFERENCE

In the notation of (55) the energy difference between two low-lying levels μ and ν as given by Eq. (37) is

$$E_\mu - E_\nu = E_\mu^p - E_\nu^p + E_\mu^{\text{ex}} - E_\nu^{\text{ex}} + E_\mu^c - E_\nu^c + E_\mu^l - E_\nu^l + \sum_{n=2}^{\infty}(E_\mu^{(n)} - E_\nu^{(n)}) , \tag{69}$$

since V_0 and V_{kk}^p are the same for all states. ν will be taken to be the normal state. Each of the expressions $E_\mu^p - E_\nu^p$ and $E_\mu^c - E_\nu^c$ represents the difference between perturbation series that depend only on the parameter r_s, while $E_\mu^{\text{ex}} - E_\nu^{\text{ex}}$ is a single term. From (20) it follows that

$$E_\mu^p - E_\nu^p = \frac{c_{0\mu} - c_{0\nu}}{r_s^2} + O(\text{const}) , \tag{70}$$

where $c_{0\mu}$ and $c_{0\nu}$ are coefficients. In addition,

$$E_\mu^{\text{ex}} - E_\nu^{\text{ex}} = \frac{c_{1\mu} - c_{1\nu}}{r_s} \tag{71}$$

and

$$E_\mu^c - E_\nu^c = O(\text{const}, \ln r_s) . \tag{72}$$

Since the unperturbed wave functions differ only in $\mathbf{k}$ values near the Fermi surface, a computation of the difference in coefficients in (70) and (71) to any accuracy is a simple problem. The contribution $E_\mu^l - E_\nu^l$ is given by the perturbation series

$$E_\mu^l - E_\nu^l = \frac{c_{2\mu} - c_{2\nu}}{r_s}\left[\frac{m}{r_sM}\right]^{1/2} + O\left[\frac{1}{r_s}\frac{m}{r_sM}\right] , \tag{73}$$

and, finally, for small r_s and m/r_sM, as postulated in Sec. VII,

$$\sum_{n=2}^{\infty}(E_\mu^{(n)} - E_\nu^{(n)}) \rightarrow E_\mu^{(2)} - E_\nu^{(2)} \rightarrow E_\mu^{(2)e\text{-ph}} - E_\nu^{(2)e\text{-ph}} + O\left[\frac{m}{r_sM}\right]^{1/2} , \tag{74}$$

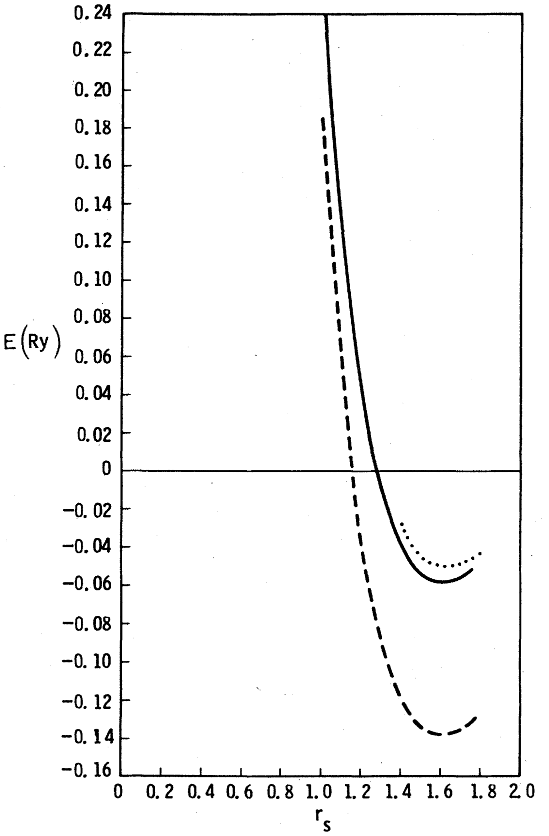

FIG. 1. Binding energy of bcc metallic hydrogen obtained by adding 1 Ry to the expansion given by Eq. (78). Solid line, the fixed lattice terms. Dashed line, the total energy with the constant C taken to be 6. Dotted line, original calculation of E. Wigner and H. B. Huntington [J. Chem. Phys. 3, 764 (1935)] for a fixed lattice. The difference between the solid curve and the dashed curve is due mainly to the electron-phonon interaction. The difference is estimated to be accurate only to about 50%.

where $E^{(2)e\text{-ph}}$ is evaluated in the approximation (50). From the discussion of the preceding section, $E^{(2)e\text{-ph}}$ leads to a term proportional to $(m/r_sM)^{1/2}$, but for states very close to the normal state a term with approximate r_s^{-1} dependence also appears. Thus, in general, the second-order electron-phonon energy should be taken together with the exchange energy to fully ensure that all r_s^{-1} dependence is accounted for.

For the complete expansion of $E_\mu - E_\nu$ one again obtains two series: one for the fixed lattice and the other for the lattice dynamics, and

$$E_\mu - E_\nu = \frac{c_{0\mu}-c_{0\nu}}{r_s^2} + \frac{c_{1\mu}-c_{1\nu}}{r_s} + O(\text{const}, \ln r_s) + \frac{c_{2\mu}-c_{2\nu}}{r_s}\left[\frac{m}{r_sM}\right]^{1/2} + (E_\mu^{(2)} - E_\nu^{(2)}) + \cdots , \tag{75}$$

where the ellipsis indicates smaller terms for the second series. Since terms given by the coefficients c_0 and c_2 are simply the difference in the unperturbed energies ε, (75) can be rewritten as

$$E_\mu - E_\nu = \varepsilon_\mu - \varepsilon_\nu + E_\mu^{\text{ex}} - E_\nu^{\text{ex}} + E_\mu^{(2)} - E_\nu^{(2)} + O(\text{const}, \ln r_s) + \cdots , \tag{76}$$

where, for two states with no phonons, $\varepsilon_\mu - \varepsilon_\nu = \varepsilon_{k'} - \varepsilon_k$ since the zero-point energy is the same. Denoting the energy difference with the normal state by Δ, keeping only the first two terms in the fixed lattice series and the first relevant term for the lattice dynamics, one obtains (for small r_s and m/r_sM)

$$\Delta E \approx \Delta\varepsilon_k + \Delta E^{\text{ex}} + (\Delta E^{(2)e\text{-ph}})_{m/r_sM \ll 1} . \tag{77}$$

Thus for high density and heavy mass, the right-hand side of (77) must be positive for all other states if the normal state is the ground state of the system. It will be shown in a later calculation that this is not the case.

X. SUMMARY

Time-independent perturbation theory has been used to develop the energy for a system of electrons and nuclei whereby the energy levels for a specified lattice are given in terms of two parameters: the parameter r_s and the ratio m/M of the electron to nuclear mass, with the independent parameters taken to be r_s and m/r_sM. The expansion is made with a basis formed from oscillator functions and Slater determinants of plane waves, and the result is simplified by isolating, within a Rayleigh-Schrödinger—type expansion, three subseries which correspond to the energy levels of known simpler systems. The three subseries give (a) the energy of a lattice of nuclei vibrating in a uniform background charge, (b) the energy of noninteracting electrons moving in a periodic potential, and (c) the correlation energy of an electron gas. The isolation of (a) and (b) is purely a matter of convenience, while that for (c) is necessary, since the series for the electron-gas correlation energy has meaning only when summed to all orders. The remaining part of the perturbation series is evaluated through second order, where contributions arise from the electron-phonon interaction and the periodic potential. From the physical nature of the problem it is assumed that the summation of the remaining terms from third order to infinity is finite, and it is assumed with partial proof that this sum corresponds to terms of higher order than are found in the leading terms in second order. No use is made of the adiabatic approximation[13] nor of self-consistent fields or dielectric constants. The importance of using bare phonons rather than screened phonons in the perturbation expansion is pointed out.

An expansion has been made for the normal state which gives quite reasonable results near the equilibrium density, as shown in Fig. 1. For a body-centered-cubic lattice the energy of this state (in rydbergs per electron) is given by

$$\frac{E}{N}=\frac{2.21}{r_s^2}-\frac{2.708}{r_s}-0.187+0.0622\ln r_s-0.053r_s$$

$$+0.018r_s\ln r_s+O(r_s^2,r_s^2\ln r_s)+\frac{2.65}{r_s}\left[\frac{m}{r_sM}\right]^{1/2}$$

$$-C\left[\frac{m}{r_sM}\right]^{1/2}+\cdots\,, \qquad (78)$$

with $C\sim 6$. The group of terms depending only on r_s is the energy for a fixed lattice, and the terms in $(m/r_sM)^{1/2}$ come from the nuclear vibrations. The latter terms result from the ordinary zero-point motion (the $r_s^{-3/2}$ term), and from two second-order perturbations involving the electron-phonon interaction (the $r_s^{-1/2}$ term). At the equilibrium value $r_s\approx 1.6$, the second term in the lattice-dynamics series is larger than the first, but the same is true of the fixed lattice series. The terms denoted by an ellipsis are expected to be smaller. Although the value of C is not very accurate, it is clear from Fig. 1 that the electron-phonon interaction has a significant effect on the binding energy.

The perturbation expansions for a pair of levels may be subtracted to give an expansion for the difference between two low-lying states. However, the form given by Eq. (78) is unique to the spherical normal state, and for states lying very close to the normal state a term independent of m/M can also appear in the second group of terms. Thus it is not proper to include higher orders for the fixed lattice without considering similar terms due to the nuclear vibrations. A condition under which the normal state is the ground state of the system is proposed in Eq. (77).

APPENDIX: ESTIMATE OF THE MAGNITUDE OF THE ELECTRON-PHONON TERM FOR THE NORMAL STATE

For values $\mathbf{p}'$ and $\mathbf{p}$ where $\mathbf{p}'-\mathbf{p}$ falls in the first Brillouin zone, $\mathbf{K}$ must be set equal to zero, and $\mathbf{p}'-\mathbf{p}=\boldsymbol{\kappa}/k_F$. The factor

$$\left|\frac{\mathbf{p}'-\mathbf{p}}{|\mathbf{p}'-\mathbf{p}|}\cdot\mathbf{v}\right|^2$$

is then nearly unity for the approximately longitudinal mode, and quite small for the modes which are approximately transverse (in the case of small $\mathbf{p}'-\mathbf{p}$ the modes approach longitudinal and transverse polarization, and the cosine of the angle made with $\mathbf{v}$ vanishes more rapidly than ω for the transverse case); therefore it follows that only the mode which is nearly longitudinal need be considered in this region. For values of $\mathbf{p}'$ and $\mathbf{p}$ where $\mathbf{K}\neq\mathbf{0}$, $\mathbf{p}'-\mathbf{p}$ is no longer in the direction of $\boldsymbol{\kappa}$, and for simplicity let the square of the cosine of the angle between $\mathbf{p}'-\mathbf{p}$ and $\mathbf{v}$ be approximated by one-half.

Although it is not implied that the energy denominator in (50) can be expanded in a power series in the small parameter $(r_sm/M)^{1/2}$, nevertheless an approximate value of the integral may be obtained by setting $(r_sm/M)^{1/2}$ equal to zero in the denominator, assuming that this leads to a finite result. Therefore, as a rough approximation, (50) becomes

$$E_\nu^{(2)e\text{-ph}}\approx-\frac{N}{\sqrt{3}\pi^4}\left[\frac{9\pi}{4}\right]^{2/3}\left[\frac{m}{r_sM}\right]^{1/2}\left[\int_{p<1}d\mathbf{p}\int_{\substack{p'>1\\ \mathbf{K}=0}}d\mathbf{p}'\frac{\omega(01)}{\omega(\boldsymbol{\kappa}1)}\frac{1}{|\mathbf{p}'-\mathbf{p}|^2(p'^2-p^2)}\right.$$

$$\left.+\tfrac{1}{2}\sum_s\int_{p<1}d\mathbf{p}\int_{\substack{p'>1\\ \mathbf{K}\neq0}}d\mathbf{p}'\frac{\omega(01)}{\omega(\boldsymbol{\kappa}s)}\frac{1}{|\mathbf{p}'-\mathbf{p}|^2(p'^2-p^2)}\right]. \qquad (\mathrm{A1})$$

Since, in the $\mathbf{K}=\mathbf{0}$ region, $\omega(01)/\omega(\boldsymbol{\kappa}1)$ approaches unity as $\mathbf{p}'-\mathbf{p}$ approaches zero, and since, in the $\mathbf{K}\neq\mathbf{0}$ region, $1/\omega(\boldsymbol{\kappa}s)$ is integrable about $\boldsymbol{\kappa}=\mathbf{0}$, the integrals in (A1) are indeed finite. In order to estimate these terms, let $\omega(01)/\omega(\boldsymbol{\kappa}s)$ be replaced by its average value, and, finally, let the volume of $\mathbf{p}$ space where $\mathbf{K}=\mathbf{0}$ be neglected. The factor inside the large parentheses in (A1) becomes, in this approximation,

$$\tfrac{1}{2}\sum_s\left\langle\frac{\omega(01}{\omega(\boldsymbol{\kappa}s)}\right\rangle\int_{p<1}d\mathbf{p}\int_{p'>1}d\mathbf{p}'\frac{1}{|\mathbf{p}'-\mathbf{p}|^2(p'^2-p^2)}\,,$$

where the sixfold integration can be shown to give the value π^4. One obtains from this rough estimate

$$E_\nu^{(2)e\text{-ph}}\approx-9N\left[\frac{m}{r_sM}\right]^{1/2}\approx-\frac{0.2N}{r_s^{1/2}}\,, \qquad (\mathrm{A2})$$

with the last expression evaluated for the proton mass. The principal contribution arises from the transverse modes (about 80% in this estimate). A more accurate result can obviously be obtained from numerical integration. The sum of (A2) with the value estimated for the mixed term in the text gives

$$E_\nu^{(2)}\approx-6.4N\left[\frac{m}{r_sM}\right]^{1/2}. \qquad (\mathrm{A3})$$

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[4] P. B. Allen and B. Metrović, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1982), Vol. 37, p. 1.

[5] W. J. Carr, Jr., Phys. Rev. **128**, 120 (1962).

[6] It has been pointed out by G. J. Hatton [Phys. Rev. A **14**, 901 (1976)] that the noncrossing rule does not generally apply even for a molecular system. However, the important point for a many-body system is not whether levels actually cross, but whether the perturbation series labeled by a given unperturbed state applies on either side of a real or imagined crossing, allowing a smooth connection between the two sides.

[7] See W. J. Carr, Jr., Phys. Rev. **122**, 1437 (1961), for a tabulation of frequencies and polarization vectors for a bcc lattice. Although the frequencies apply for a different problem, their ratios are applicable here.

[8] The discussion here is restricted to occupied regions of $\mathbf{k}$ space which do not touch the zone boundary.

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[13] However, in some sense the assumption of small values for m/M implies that the adiabatic approximation holds.