

## Structure of matter in strong magnetic fields

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(Received 13 April 1987)

We give a detailed presentation of Hartree-Fock calculations of atoms and molecular chains in  $10^{12}$  G magnetic fields, as are supposed to exist on the surface of neutron stars. These calculations are the first self-consistent ones treating exchange properly for atoms heavier than helium in high fields. We find that the isolated atom is energetically favored over molecular chains for  $Z > 2$  at fields greater than  $1 \times 10^{12}$  G and for  $Z > 4$  at fields greater than  $5 \times 10^{12}$  G. These results indicate that matter on the surface of neutron stars is bound very weakly, if at all.

### I. INTRODUCTION

The state of matter in the presence of strong magnetic fields ( $B = 10^{12} - 10^{13}$  G) is relevant to neutron star studies,<sup>1-4</sup> apart from its intrinsic interest. Particularly important is whether the surface of a neutron star is a solid or a gas. The optical properties of such a star, and the heating of its surface, are related to this question.<sup>5</sup>

In this paper we present a detailed discussion of variational Hartree-Fock calculations for matter in strong magnetic fields, following a summary of our results.<sup>6</sup> We calculate the single-particle and binding energies of both isolated atoms and single linear chains of atoms. The latter largely determine the structure of the solid phase, as we discuss below.

Our calculations are the first self-consistent ones treating exchange properly for atoms heavier than helium<sup>7</sup> in high fields, and are therefore particularly important for neutron star surfaces, where the dominant material is believed to be iron. Within our approximations, we find that for elements with atomic number  $Z > 2$  at  $B_{12} = 1$  (and  $Z > 4$  at  $B_{12} = 5$ ), the isolated atom is energetically favored over the molecular chain (here, and in the following, we use the convention  $B_{12} = B/10^{12}$  G). This is because in strong fields all electron spins are oriented along the field. The Pauli principle implies a totally antisymmetric spatial wave function, which in turn means that the predominant zero-field bonding mechanism, where two atoms bind together in a spin-singlet spatially symmetric state, will not be effective.

Our presentation is organized as follows. In Sec. II we give a qualitative discussion of atomic structure in strong fields and introduce the relevant parameters. In Sec. III we justify our ansatz for the isolated-atom wave function: the Hartree-Fock wave function in the adiabatic approximation. From this wave function, we derive the one-dimensional Hartree-Fock equations in Sec. IV, and explain their solution. In Sec. V we explain the chain approximation for three-dimensional matter and discuss different choices for the Bloch wave functions. Section VI is analogous to Sec. IV: We derive the

Hartree-Fock equations for one-dimensional chains. The extension to infinite chains introduces complications, some of which are dealt with by the standard method of Fourier transform, while others require analytical manipulations. Numerical results are presented in Sec. VII, along with comparisons with previous calculations. For the convenience of the reader, we separated the presentation of all approximations that require physical justification (Secs. II, III, and V) from the presentation of the solutions of equations (Secs. IV and VI).

### II. BASIC CONCEPTS

The Hamiltonian of a neutral atom in a uniform magnetic field can be written as

$$\begin{aligned}
 H &= H_B + V_{eZ} + V_{ee} \\
 &= \sum_i \frac{1}{2M} \left[ \mathbf{p}_i + \frac{e}{c} \mathbf{A}_i \right]^2 + \sum_i \frac{e}{Mc} \mathbf{B} \cdot \mathbf{S}_i - Ze^2 \sum_i \frac{1}{r_i} \\
 &\quad + e^2 \sum_{i,j} \frac{1}{r_{ij}}, \quad (2.1)
 \end{aligned}$$

where the index  $i$  labels the electrons,  $Z$  is the nuclear charge, and  $\mathbf{p}$ ,  $\mathbf{r}$ , and  $\mathbf{S}$  are the momentum, position, and spin, respectively. The electron's mass and charge are  $M$  and  $-e$ , respectively, while  $\mathbf{A}$  is the electromagnetic potential of a uniform magnetic field,

$$\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}. \quad (2.2)$$

We neglect the motion of the nucleus,<sup>8</sup> incurring errors of the order of the electron-nucleus mass ratio. These are too small to affect our calculations of the cohesive energy, but since the binding energies are very large in strong fields (see below), the energies associated with the motion of the nucleus are much higher than when  $B = 0$ . Indeed, these splittings may reach several eV and the corresponding modifications of the opacities strongly change the radiation spectra, since neutron star surface temperatures are in the 1–100-eV range.<sup>3</sup>

Our discussion in this section is qualitative and we neglect the electron-electron repulsion. This latter is, in fact, dominated by the nucleus-electron attraction and we include it in Sec. III below via the mean field it creates. Our many-electron wave function is thus a Slater determinant of single-electron orbitals.

The structure of the single-electron orbitals is determined by the relative strengths of the magnetic and Coulomb interactions. When the magnetic field is very small, the Zeeman-split hydrogen atom is recovered. Our interest, however, is in the opposite extreme: strong magnetic fields perturbed slightly by the Coulomb interaction. To study this limit, we first neglect the Coulomb interactions and consider only the magnetic Hamiltonian.

The magnetic Hamiltonian is separable into three parts:

$$H_B = H_z + H_\perp + H_S. \quad (2.3)$$

Here  $H_z (= P_z^2/2M)$  governs the motion parallel to the field,  $H_\perp$  the motion perpendicular to the field, and  $H_S$  the spin degree of freedom.

The Hamiltonian  $H_\perp$  has an infinitely degenerate, discrete harmonic-oscillator spectrum

$$E_\perp = \frac{1}{2} \hbar \omega (n - m + |m| + 1), \quad n \geq 0 \quad (2.4)$$

where

$$\hbar \omega = 11.5 \text{ keV} \times B_{12}. \quad (2.5)$$

The integers  $n$  and  $m$  label the eigenfunctions of  $H_\perp$ ,

$$\psi_{mn}(\rho, \phi) = W_{mn}(\rho) e^{-im\phi}, \quad (2.6)$$

where we have introduced the usual cylindrical coordinates  $(\rho, \phi, z)$  and the Landau functions  $W_{mn}$ . We will be interested only in the form of the lowest-energy ( $n=0$ ) Landau functions

$$W_{m0}(\rho) = \frac{1}{\sqrt{2\pi} |m|!} \left[ \frac{\rho}{\sqrt{2}} \right]^{|m|} e^{-\rho^2/4}. \quad (2.7)$$

These are peaked at  $\rho_m = \hat{\rho} \sqrt{2m+1}$ . Here, and in the following, the unit of length is the Landau radius

$$\hat{\rho} = (\hbar c / eB)^{1/2} = 2.5 \times 10^{-10} \text{ cm} \times B_{12}^{-1/2}.$$

The one-body eigenfunctions of  $H_B$  are products of eigenfunctions of  $H_z$ ,  $H_\perp$ , and  $H_S$ ,

$$X_{mkS} = W_{m0}(\rho) e^{-im\phi} e^{ikz} |S_z\rangle. \quad (2.8)$$

The perturbing nucleus-electron attraction breaks the degeneracy of  $m$ , since lower- $m$  orbitals lie closer to the nucleus. However, the  $z$  component of the orbital angular momentum,  $L_z (= -m\hbar)$  is conserved by the spherically symmetric attraction, so that orbitals with different Landau indices,  $m$ , are not mixed. The spin projection  $S$  also remains a good quantum number.

The nuclear Coulomb potential can be treated as a perturbation as long as its matrix elements are much smaller than the excitation energy of orbitals with  $n > 1$ ,

$$\langle V_{eZ} \rangle \sim \frac{Ze^2}{\hat{\rho}} \ll \hbar \omega. \quad (2.9)$$

This condition can be shown to be equivalent to  $B > Z^2 B_C$ , where

$$B_C = 2.3 \times 10^9 \text{ G}.$$

For iron the critical field strength is  $10^{12}$  G; for higher field strengths,  $n$  is a good quantum number, and the wave function is separable.

The nuclear Coulomb attraction localizes the electrons in the direction along the magnetic field. The plane wave is replaced by a real, localized function

$$e^{ikz} \rightarrow f_{nm\nu}(z), \quad (2.10)$$

$$\int f_{nm\nu}^*(z) f_{nm\nu'}(z) dz = \delta_{\nu\nu'},$$

where the index  $\nu$  labels the number of nodes. In the following, we omit the index  $n$  from  $f_{nm\nu}$ , as only  $n=0$  states are considered. Higher- $n$  orbitals have large energies ( $\geq \hbar \omega$ ) and are not populated at the ground state. The Hamiltonians  $H_\perp$  and  $H_z$  are affected differently by the perturbation since the former has a discrete spectrum.

It can be shown that in very strong fields the energy required to put the electron in a higher node state ( $\nu > 0$ ) is larger than the energy required to put it in higher Landau orbitals,  $m > 0$ .<sup>1</sup> Hence, the electrons of a general atom in strong fields will occupy the states  $\{m=0, \dots, Z-1; \nu=0\}$ . For intermediate-strength fields, the inner Landau orbitals are populated by several electrons, each with different  $\nu$  quantum numbers. For example, the first six Landau orbitals of iron at  $10^{12}$  G are each occupied by two or more electrons.

Although the ansatz (2.8) is strictly valid only for very strong fields, we can use it to calculate the cohesive energies, even at moderate field strengths,  $B \sim Z^2 B_C$ . The Coulomb perturbation will mix higher- $n$  states only for the inner- $m$  orbitals. These, however, are close to the nuclei and will be largely unmodified when the atoms join together to form a chain, so that their contributions to the cohesive energy (as a function of separation) will almost cancel. For the same reason, we can ignore relativistic effects, which are much smaller than naively expected because the relativistic wave function is also separable to perpendicular and parallel components.<sup>9</sup> Rather than being proportional to  $\hbar \omega / Mc^2$ , the relativistic corrections are proportional to  $v_{eZ} / Mc^2$ , where  $v_{eZ}$  is the attraction of the nucleus felt by a single electron. From Eqs. (2.7) and (2.9) we deduce that even for the innermost orbital of iron,  $m=0$ , the corrections are less than 4% for  $B = 10^{13}$  G, with much smaller corrections for the other electrons.

### III. THE ANSATZ FOR ISOLATED ATOMS

Our main goal is to calculate the cohesive energy—the difference between the binding energy of isolated atoms and the maximum binding energy of atoms in crystals. As these two energies are comparable, a meaningful calculation of their difference (or at least its sign,

indicating whether or not crystals are bound) requires that errors in our calculations of the binding energies be smaller than the cohesive energy. Experience with zero-field calculations leads us to expect that, if the atoms are bound, the cohesive energy is a few percent of the total energy. Our nominal goal in the binding energy calculations is therefore 1%. Indeed, in the event that we find no binding with calculations of this accuracy, then the crystals are probably not bound by more than this uncertainty.

We use a Hartree-Fock approach in our calculations, less restricted (and hence more accurate) than a previous variational calculation.<sup>10</sup> This problem has also been studied using a density-functional formalism with the form of the exchange energy taken from studies of uniform zero-field electron gas.<sup>11-13</sup> This is questionable since electron densities for strong fields are localized near the nucleus, and the presence of the magnetic field modifies the exchange correlation. Indeed, we later (Sec. VII) compare the Hartree-Fock and density-functional results and find that the latter overestimate the exchange energies by more than 30%, or 2% of the total binding energy.

In the Hartree-Fock method, the wave function is approximated by a Slater determinant of single-electron orbitals. The optimal set of these latter is determined by solving the variational equation

$$\frac{\delta}{\delta\chi} \left[ \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right] = 0. \quad (3.1)$$

Of course, this determinant does not include dynamical electron-electron correlations, and the interelectron repulsion is included only through the mean field. In strong fields, the one-body orbitals are separable [Eq. (2.8)]; the only unknowns are the one-dimensional functions  $f_{m\nu}(z)$ . The Hartree-Fock equations therefore reduce to a set of one-dimensional (coupled) equations

$$\langle H_B \rangle = \langle H_z \rangle = \frac{\hbar^2}{2M} \sum_{m,\nu} \int |f'_{m\nu}(z)|^2 dz, \quad (4.2a)$$

$$\langle V_{eZ} \rangle = -\frac{Ze^2}{\hat{\rho}} \sum_{m,\nu} \int V_m(z) |f_{m\nu}(z)|^2 dz, \quad (4.2b)$$

$$\langle V_{ee} \rangle = \frac{e^2}{\hat{\rho}} \sum_{m,\nu,m',\nu'} \left[ \int D_{mm'}(z-z') |f_{m\nu}(z)|^2 |f_{m'\nu'}(z')|^2 - E_{mm'}(z-z') f_{m\nu}(z) f_{m'\nu'}(z') f_{m'\nu'}^*(z) f_{m\nu}^*(z') \right] dz dz'. \quad (4.2c)$$

In these expressions the nuclear, direct, and exchange kernels are

$$V_m(z) = \int \frac{|W_{m0}(\rho)|^2}{\sqrt{\rho^2+z^2}} \rho d\rho d\phi = \int \frac{e^{-\rho^2/2} \rho^{2m+1}}{2^m m! \sqrt{\rho^2+z^2}} d\rho, \quad (4.3a)$$

$$D_{mm'}(z-z') = \int \frac{e^{-[(\rho^2+\rho'^2)/2]} \rho^{2m+1} (\rho')^{2m'+1}}{2^{m+m'} m! m'! \sqrt{(\rho-\rho')^2+(z-z')^2}} d\rho d\rho', \quad (4.3b)$$

$$E_{mm'}(z-z') = \int \frac{e^{-[(\rho^2+\rho'^2)/2]} (\rho\rho')^{m'+m+1} e^{-i(m-m')(\phi-\phi')}}{2^{m+m'} m! m'! \sqrt{(\rho-\rho')^2+(z-z')^2}} d\rho d\rho' \frac{d\phi}{2\pi} \frac{d\phi'}{2\pi}, \quad (4.3c)$$

$$\frac{\delta}{\delta f_{m\nu}(z)} \left[ \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right] = 0. \quad (3.2)$$

Most of the error in zero-field Hartree-Fock calculations is associated with symmetrization of the spatial wave function of electrons in a spin-singlet state. In the exact solution, the electron-electron repulsion depletes the wave function for small relative distances (Coulomb hole), while naive symmetrization of the orbitals causes the opposite effect. For electrons in a spin-triplet state, antisymmetrization of the spatial wave function creates a hole that imitates this Coulomb effect. In strong fields, all spins are aligned antiparallel to the field, so that all electron pairs are spin triplet and the Slater determinant reduces to a totally antisymmetric spatial determinant. The error is therefore expected to be significantly smaller than the 1% value characteristic of zero-field calculations.<sup>8</sup>

As is usual in Hartree-Fock, our calculations use an approximate wave function but leave the Hamiltonian intact. By the variational principle, first-order errors in the wave function induce only second-order errors in the variational energy  $\langle H \rangle$ . Moreover, successive improvements in the energy can be calculated systematically. This is clearly an advantage over those methods that approximate the Hamiltonian. While the parameters in these latter can be fixed by fitting to zero-field experimental data, no such calibration is possible for strong fields.

#### IV. CALCULATIONS FOR ISOLATED ATOMS

The expectation value of the Hamiltonian (2.1) in the Hartree-Fock determinantal wave function [composed of orbitals (2.8)] is

$$E = \langle H \rangle = \langle H_B \rangle + \langle V_{eZ} \rangle + \langle V_{ee} \rangle, \quad (4.1)$$

where

and we used the fact that for the  $n=0$  orbitals,  $\langle H_z \rangle = -\langle H_\perp \rangle$ .

The Hartree-Fock equations for the ground-state orbitals, (3.2), are equivalent to

$$\frac{\delta \langle \Psi | H | \Psi \rangle}{\delta f_{m\nu}^*(z)} = \epsilon_{m\nu} \frac{\delta \langle \Psi | \Psi \rangle}{\delta f_{m\nu}^*(z)}, \quad (4.4)$$

where the Lagrange multipliers ensuring the orthogonality relations (2.10) are the single-particle energies  $\{\epsilon_{m\nu}\}$ . The explicit form of these equations follows from (4.1)–(4.3):

$$\left[ -\frac{\hbar^2}{2M} \frac{d^2}{dz^2} - \frac{Ze^2}{\hat{\rho}} V_m(z) + \frac{e^2}{\hat{\rho}} K_m(z) - \epsilon_{m\nu} \right] f_{m\nu}(z) = \frac{e^2}{\hat{\rho}} J_{m\nu}(z), \quad (4.5)$$

where the direct and exchange potentials are

$$K_m(z) \equiv \sum_{m',\nu'} \int D_{mm'}(z-z') |f_{m'\nu'}(z')|^2 dz', \quad (4.6a)$$

$$J_{m\nu}(z) \equiv \sum_{m',\nu'} f_{m'\nu'}(z) \int E_{mm'}(z-z') f_{m'\nu'}^*(z') f_{m\nu}(z') dz'. \quad (4.6b)$$

The Hartree-Fock equations (4.5) are nonlinear and coupled. We solve them by iteration: The direct and exchange potentials  $K$  and  $J$  are calculated from the “old” wave functions, and the equations (4.5) are then solved for the “new” wave functions.

We expect the orbitals to decay exponentially for large  $z$ , so that we replace the line  $(-\infty, \infty)$  by a large cell  $[-l, l]$  and demand that the orbitals vanish on the boundaries of this cell. We find that  $l$  has to be at least as large as  $50\hat{\rho}$  for convergence. The differential equations and the quadratures are discretized in a uniform mesh spanning the cell. Typically, a few hundred points are sufficient for convergence. We note that the energy is invariant with respect to reflections through the plane  $z=0$ , so that the orbitals have a definite symmetry under  $z \rightarrow -z$ . The wave functions  $\{f_{m\nu}\}$  for the isolated atom can be chosen to be real, in contrast to those of a crystal, which must satisfy the intrinsically complex Bloch condition  $f(x+a) = e^{ika} f(x)$ .

We evaluate the convolution integrals in (4.6) by Fourier transforms. Direct numerical evaluation of the kernels in momentum space is complicated by their  $1/z$  falloff, so that we have instead used the analytic expressions<sup>7</sup>

$$V_m(z) = \int_0^\infty L_m \left[ \frac{q^2}{2} \right] e^{-q^2/2} e^{-q|z|} dq, \quad (4.7a)$$

$$D_{mm'}(z) = \int_0^\infty L_m \left[ \frac{q^2}{2} \right] L_{m'} \left[ \frac{q^2}{2} \right] e^{-q^2} e^{-q|z|} dq, \quad (4.7b)$$

$$E_{mm'}(z) = \int_0^\infty \left[ \frac{m!}{m'} \right] \left[ \frac{q^2}{2} \right]^{m'-m} \left[ L_{m'-m} \left[ \frac{q^2}{2} \right] \right]^2 \times e^{-q^2} e^{-q|z|} dq, \quad (4.7c)$$

where  $L_n$  is the Laguerre polynomial,  $L_n^{(\alpha)}$  is the associated Laguerre polynomial, and we can assume  $m' > m$  with no loss of generality. (These relations are established in Ref. 7.)

From the definition of the Laguerre polynomials, it is easy to show that the Fourier transform of the nuclear kernel is

$$\begin{aligned} V_m(q) &\equiv \int_{-\infty}^\infty e^{iqz} V_m(z) dz \\ &= \int_0^\infty \frac{y^m}{(y+q^2/2)^{m+1}} e^{-y} dy \\ &= \frac{\sqrt{2}m!}{|q|} e^{q^2/4} U_{-1/2-m,0} \left[ \frac{q^2}{2} \right], \end{aligned} \quad (4.8)$$

where  $U$  is the Whittaker function, and the last equality follows from Eq (13.1.33) in Ref. 14. For small  $q$  we evaluate the Whittaker function from its expansion in  $q^{2k} \ln q$ ;<sup>15</sup> for larger  $q$  we integrate (4.8) numerically, by a change of variables,

$$y \rightarrow t = \frac{y}{y+y_{\max}}, \quad (4.9)$$

where  $y_{\max}$  is the point where the integrand reaches its maximum

$$y_{\max} = \frac{1}{2} \left\{ \left[ \left[ \frac{q^2}{2} + 1 \right] + 2mq^2 \right]^{1/2} - \left[ \frac{q^2}{2} + 1 \right] \right\}, \quad (4.10)$$

We evaluate the direct and exchange kernels in momentum space by expanding the products of the polynomials in (4.7b) and (4.7c) as sums of Laguerre polynomials,

$$L_m \left[ \frac{y}{2} \right] L_{m'} \left[ \frac{y}{2} \right] = \sum_{s=0}^{m+m'} d_s(m, m') L_s(y), \quad (4.11a)$$

$$\frac{m!}{m'} \left[ \frac{y}{2} \right]^{m'-m} \left[ L_{m'-m} \left[ \frac{y}{2} \right] \right]^2 = \sum_{s=0}^{m+m'} g_s(m, m') L_s(y), \quad (4.11b)$$

where the  $d$ 's and  $g$ 's are constant coefficients (i.e., independent of  $y$ ). The direct kernels are then

$$D_{mm'}(z) = \frac{1}{\sqrt{2}} \sum_{s=0}^{m+m'} d_s(m, m') V_s \left[ \frac{z}{\sqrt{2}} \right], \quad (4.12a)$$

$$D_{mm'}(q) = \sum_{s=0}^{m+m'} d_s(m, m') V_s(q\sqrt{2}), \quad (4.12b)$$

with a similar expression for the exchange kernels. The expansions (4.11) are essential for the calculation of the chain energy given in Sec. VI.

We calculate the coefficients  $d$  and  $g$  by the Gram-Schmidt procedure. This involves delicate cancellations between different terms, and so can be subject to numerical instabilities. To overcome this problem, we recast (4.11) in the form

$$\left[ 2^m \tilde{L}_m \left( \frac{y}{2} \right) \right] \left[ 2^{m'} \tilde{L}_{m'} \left( \frac{y}{2} \right) \right] = \sum_{s=0}^{m+m'} \tilde{d}_s(m, m') \tilde{L}_s(y), \quad (4.13)$$

where

$$\tilde{L}_m(y) \equiv m! L_m(y) = e^y \frac{d^m (y^m e^{-y})}{dy^m}, \quad (4.14)$$

$$\tilde{d}_s(m, m') \equiv \frac{2^{m+m'} (m+m')!}{s!} d_s(m, m'). \quad (4.15)$$

These polynomials have integer coefficients, and their leading coefficient is  $\pm 1$ ; it follows that the  $\tilde{d}$ 's and the  $\tilde{g}$ 's are integers, and that the Gram-Schmidt reduction of (4.13) involves only integers. We evaluated exactly all coefficients with indexes  $m, m' \leq 50$ ,  $s \leq 100$  using a code written in integer arithmetic.

To begin the iterative solution of the Hartree-Fock equations, we took initial wave functions of the form

$$f_{m\nu} \propto z^\nu \exp(-a_{m\nu} |z|), \quad (4.16)$$

as were assumed in previous restricted variational studies.<sup>10,16</sup> We used the parameters  $\{a_{m\nu}\}$  as given in Ref. 16 but checked that our converged solutions were insensitive to wide variations in these parameters.

As we do not know *a priori* which  $Z$  one-body states are occupied in the optimal Slater determinant, we had to calculate the single-particle energies of a large number of states at each iteration and then occupy those with lowest energy. In our calculations of atoms through iron,  $Z \leq 26$ , it is sufficient to include all zero-node states with  $0 \leq m \leq Z-1$ , together with one- and two-node states for  $m \leq 10$ . We verified that the converged results are not affected by the choice of initially occupied orbitals. The occupied orbitals in the optimal solutions for various field strengths are presented below in Sec. VII.

## V. THE ANSATZ FOR MOLECULAR CHAINS

In this section we describe our ansatz for the structure of matter in strong fields. We follow earlier approaches in assuming linear chains of equispaced stationary nuclei (charge  $Z$ , spacing  $a$ ), oriented along the magnetic field;<sup>1,10</sup> the equilibrium spacing is found by minimizing the energy per atom as a function of  $a$ . As explained in the Introduction, chains are isolated from one another by Pauli repulsion, as electrons are constrained to stay in the Landau orbitals. Thus, electrons move freely along the field, but are localized in the transverse directions. In other words, matter in strong fields is a conductor along the field lines but an insulator perpendicular to the field, like a classical plasma in a magnetic field.

Since the chain-chain interaction does not significantly perturb the structure of the chain, it can be calculated with the wave functions of an isolated chain. The numerical study in Ref. 12 shows that the additional attraction associated with this interaction is very small

(less than 1% of the binding energy). With the curves of energy versus spacing used in Ref. 12, this attraction will bind iron weakly. However, our curves presented below are much stiffer, and this attraction will therefore bind iron very weakly, if at all.

Our variational wave function for electrons in a chain is similar to the isolated-atom ansatz described above. We assume a Slater determinant composed of single-particle wave functions. In the adiabatic approximation the single-particle orbitals are

$$\psi_{m\nu k}(\rho, \phi, z) = W_{m0}(\rho, \phi) f_{m\nu k}(z) |S_z = \frac{1}{2}\rangle, \quad (5.1)$$

where the node index  $\nu$  is supplemented by the continuous quasimomentum index  $k$ . These latter fill continuous bands

$$|k| \leq \frac{\sigma_{m\nu} \pi}{a}, \quad (5.2)$$

where we introduced the band-occupation index  $\sigma_{m\nu}$ . The periodicity imposes the Bloch condition

$$f_{m\nu k}(z+a) = f_{m\nu k}(z) e^{ika}. \quad (5.3)$$

We must, of course, specify the  $k$  dependence of  $f_{m\nu k}$ , compatible with the orthogonality of different orbitals. As a corollary of the Bloch condition, two orbitals with quasimomenta  $k, k'$  that differ by noninteger multiples of  $2\pi/a$  [ $k \neq k' \pmod{2\pi/a}$ ] will be orthogonal naturally:

$$\begin{aligned} & \int_{-\infty}^{\infty} f_{m\nu k'}^*(z) f_{m\nu k}(z) dz \\ &= \left[ \sum_{n=-\infty}^{\infty} e^{i(k-k')na} \right] \int_{-a/2}^{a/2} f_{m\nu k'}^*(z) f_{m\nu k}(z) dz \\ &= 0 \text{ if } k \neq k' \pmod{\frac{2\pi}{a}}, \end{aligned} \quad (5.4)$$

but we must impose orthogonality for  $k = k' \pmod{2\pi/a}$ .

We adopt the "plane-wave" ansatz,

$$f_{m\nu k}(z) = f_{m\nu}(z) e^{ikz}, \quad (5.5)$$

where the  $f_{m\nu}$  are  $k$ -independent periodic functions with period  $a$ , to be determined by the variational equations (Sec. III). As in the isolated-atom case, the functions must be orthogonal over the unit cell

$$\int_{-a/2}^{a/2} f_{m\nu'}^*(z) f_{m\nu}(z) dz = \delta_{\nu\nu'}. \quad (5.6)$$

In addition, we must impose

$$\begin{aligned} & \int_{-a/2}^{a/2} f_{m\nu'}^*(z) f_{m\nu}(z) e^{i(k-k')z} dz = 0 \\ & \text{if } (k-k') = \frac{2n\pi}{a}, \quad n \neq 0, \end{aligned} \quad (5.7)$$

which is most simply done by ensuring that the condition on the right will never be satisfied, i.e., by choosing

$$\sigma_{m\nu} < 1. \quad (5.8)$$

An alternative choice for the  $k$  dependence of the orbitals that allows the use of high quasimomenta,  $\sigma_{m\nu} > 1$ , is a "modified plane wave"<sup>17</sup>

$$f_{mk}(z) = e^{ika \int^z |f_m|^2 dz'} f_m(z). \quad (5.9)$$

To satisfy the Pauli principle, we allow only one  $k$ -independent function,  $f_{m\nu}$ , for each Landau orbital. In the ground state, all these functions have zero nodes,  $\nu=0$ , and we omit the  $\nu$  index.

The two alternative phase factors  $ikz$  and  $ika \int |f_m|^2 dz$  have the same variation across a unit cell  $a$ . The modified phase varies most rapidly in the region of largest amplitude, unless  $f_m$  is constant (in which case the phase factors are equal); consequently, the kinetic energy associated with it is higher.  $\langle V_{eZ} \rangle$  and  $\langle V_{ee} \rangle$  depend only on the amplitude of the wave function, and therefore do not depend on the choice of phase.

The two choices of  $k$  dependence correspond to two different physical pictures. For large internuclear spacing, the  $z$ -dependent wave functions should approach the isolated-atom wave functions; in that case the plane-wave ansatz (5.5) is appropriate. Note, however, that for very large spacings the Bloch-wave ansatz is not appropriate. Lower kinetic energy is obtained by replacing the  $z$  in the phase factor with any function that varies only in the region where  $f$  is very small:

$$f_{m\nu k}(z) = f_{m\nu}(z) e^{ikg(z)}, \quad g(z+a) = a + g(z), \\ dg/dz \neq 0 \quad \text{only if } z \sim na + a/2, \\ n = 0, \pm 1, \pm 2, \dots \quad (5.10)$$

In this ansatz, the kinetic energy associated with  $g$  is proportional to

$$\int (dg/dz)^2 |f_{m\nu}(z)|^2 dz \sim |f_{m\nu}(a/2)|^2 \int (dg/dz)^2 dz,$$

and so decreases exponentially with  $a$ , rather than as a power.

The modified plane-wave choice seems more natural as an extension of a uniform matter picture ( $f_m$  constant): Higher nodes are replaced by high quasimomenta and the spectrum is continuous. In the uniform density limit, the phase factors are equal, but for slight perturbations from uniformity, only the modified plane waves can naturally accommodate the Pauli principle without artificially restricting the maximum band occupation  $\sigma_{m\nu}$  to be less than 1.

Only the plane-wave choice (5.5) allows a tractable calculation of the exchange term, and so we could not investigate the alternative. However, the latter is unlikely to give a lower energy. At every spacing, only the inner cores (low  $m$ ) have high occupations,  $\sigma_m > 1$ . Unless the spacing is small, the core orbitals in a chain will be similar to those of isolated atoms and the plane-wave choice more appropriate. For the high- $m$  orbitals the incorporation of high quasimomenta in the modified plane-wave ansatz is irrelevant, as even the zero-node

band is not filled,  $\sigma_{m0} < 1$ . Without the advantage of incorporating high  $k$ , the modified plane-wave choice is clearly inferior, as it induces higher kinetic and exchange energies.

## VI. CALCULATIONS FOR MOLECULAR CHAINS

The Hamiltonian of a chain is the periodic extension of (2.1):

$$H = H_B + V_{eZ} + V_{ee} + V_{ZZ}, \quad (6.1)$$

where  $H_B$ ,  $V_{ee}$ , and  $V_{eZ}$  are now

$$H_B = \sum_i \frac{1}{2M} \left[ \mathbf{p}_i + \frac{e}{c} \mathbf{A}_i \right]^2 - \sum_i \frac{e}{mc} \mathbf{B} \cdot \mathbf{S}_i, \quad (6.2)$$

$$V_{ee} = e^2 \sum_{\substack{i,j \\ (i < j)}} \frac{1}{r_{ij}}, \quad (6.3)$$

$$V_{eZ} = -Ze^2 \sum_i \sum_{n=-\infty}^{\infty} \frac{1}{|\mathbf{r}_i - na\hat{\mathbf{z}}|}, \quad (6.4)$$

$a$  is the internuclear spacing, and the index  $i$  labels all electrons in the chain. The new term  $V_{ZZ}$  accounts for the repulsion of different nuclei

$$V_{ZZ} = \frac{Z^2 e^2}{2} \sum_{\substack{n,n' \\ (n \neq n')}} \frac{1}{|n'a - na|}. \quad (6.5)$$

The Coulomb interactions  $V_{eZ}$ ,  $V_{ee}$ , and  $V_{ZZ}$  separately have an unphysical logarithmic divergence as the length of the chain becomes large, but since the chain is neutral, their sum is finite and nonzero.

We regularize the divergence associated with the long-range Coulomb interaction by truncating the Coulomb interaction at a range  $Na/2$  and assuming that the electron wave functions have period  $Na$ , where  $N$  is large and the limit  $N \rightarrow \infty$  is taken at the end of the calculations. An alternative regularization would be to assume a finite chain with  $N$  atoms. Both schemes give the same total energy in the large  $N$  limit, but give different (divergent) values for each of the three components,  $V_{eZ}$ ,  $V_{ee}$ , and  $V_{ZZ}$ . The divergences in each term are independent of the regularization scheme, but an inconsistent evaluation of the finite parts will produce an error. This was apparently the case in Ref. 18, which obtained an erroneously large cohesive energy.

As a result of the periodic boundary conditions, the range of the  $z$  integrals analogous to (4.2) is restricted to  $-Na/2 < z < Na/2$  and  $-Na/2 + z < z' < Na/2 + z$ . Similar restrictions hold for the summations over nuclei. In addition, the Bloch momenta are discrete:

$$k = 0, \pm \frac{2\pi}{Na}, \pm \frac{4\pi}{Na}, \dots, \pm \frac{2N_{m\nu}\pi}{Na}, \quad (6.6)$$

where the definition of the occupation factor (5.2) implies  $N_{m\nu} = N\sigma_{m\nu}/2$ .

With our plane-wave ansatz, the various terms in the total energy are given by

$$\begin{aligned} \langle H_B \rangle &= \left\langle \frac{P_z^2}{2M} \right\rangle \\ &= \frac{\hbar^2}{2M} \sum_{m,v,k} \left[ k^2 + \int_{|z| < Na/2} |f'_{m\nu}(z)|^2 dz \right], \end{aligned} \quad (6.7a)$$

$$\langle V_{eZ} \rangle = -\frac{Ze^2}{\hat{\rho}} \sum_{m,v,k} \int_{|z| < Na/2} V_m(z) |f_{m\nu}(z)|^2 dz, \quad (6.7b)$$

$$\begin{aligned} \langle V_{ee} \rangle &= \frac{e^2}{\hat{\rho}} \sum_{\substack{m,v,k \\ m',v',k'}} \int_{\substack{|z| < Na/2 \\ |z-z'| < Na/2}} [D_{mm'}(z-z') |f_{m\nu}(z)|^2 |f_{m'\nu'}(z')|^2 \\ &\quad - G_{mm'}(z-z') f_{m'\nu'}(z) f_{m\nu}(z') f_{m\nu}^*(z) f_{m'\nu'}^*(z') e^{i(k-k')(z-z')}] dz dz', \end{aligned} \quad (6.7c)$$

$$\langle V_{ZZ} \rangle = \frac{NZ^2 e^2}{a\hat{\rho}} \sum_{n=1}^{N/2} \frac{1}{n}, \quad (6.7d)$$

with the nuclear, direct, and exchange kernels as defined in (6.1). From the periodicity of the wave functions and from (6.6), it follows that the energies per unit cell are

$$E_B \equiv \langle H_B \rangle / N = \frac{\hbar^2}{2M} \sum_{m,v} \sigma_{m\nu} \left[ \frac{1}{3} \left[ \frac{\pi \sigma_{m\nu}}{a} \right]^2 + \int |f'_{m\nu}(z)|^2 dz \right], \quad (6.8a)$$

$$E_{eZ} = -\frac{Ze^2}{\hat{\rho}} \sum_{m,v} \sigma_{m\nu} \int \tilde{V}_m(z) |f_{m\nu}(z)|^2 dz, \quad (6.8b)$$

$$\begin{aligned} E_{ee} &= \frac{e^2}{\hat{\rho}} \sum_{m,v,m',v'} \sigma_{m\nu} \sigma_{m'\nu'} \int [\tilde{D}_{mm'}(z-z') |f_{m\nu}(z)|^2 |f_{m'\nu'}(z')|^2 \\ &\quad - \tilde{G}_{m\nu m'\nu'}(z-z') f_{m'\nu'}(z) f_{m\nu}(z') f_{m\nu}^*(z) f_{m'\nu'}^*(z')] dz dz', \end{aligned} \quad (6.8c)$$

where all integrals are now taken over the unit cell  $[-a/2, a/2]$ . The modified kernels are

$$\tilde{V}_m(z) = \sum_{n=-N/2}^{N/2} V_m(z_n), \quad (6.9a)$$

$$\tilde{D}_{mm'}(z) = \sum_{n=-N/2}^{N/2} D_{mm'}(z_n), \quad (6.9b)$$

$$\begin{aligned} \tilde{G}_{m\nu m'\nu'}(z) \\ &= \sum_{n=-\infty}^{\infty} \frac{\sin(\sigma_{m\nu} z_n \pi / a) \sin(\sigma_{m'\nu'} z_n \pi / a)}{\sigma_{m\nu} z_n \pi / a \sigma_{m'\nu'} z_n \pi / a} G_{mm'}(z_n), \end{aligned} \quad (6.9c)$$

where  $z_n \equiv z - na$ , and the modified exchange kernels depend on the nodes  $\nu, \nu'$  through their dependence on the occupation numbers. For large  $z$ , the Bloch factor in (6.9c) falls as  $z^{-2}$ , so that the sum is convergent; we replace its limits by  $\pm N/2$  by  $\pm \infty$ .

As in Sec. III, we obtain the Hartree-Fock equations by variation of the total energy. It is easy to show that the resulting equations are

$$\begin{aligned} \left\{ \frac{\hbar^2}{2M} \left[ -\frac{d^2}{dz^2} + \frac{1}{3} \left[ \frac{\sigma_{m\nu} \pi}{a} \right]^2 \right] - \frac{Ze^2}{\hat{\rho}} \tilde{V}_m(z) \right. \\ \left. + \frac{e^2}{\hat{\rho}} \tilde{K}_m(z) - \epsilon_{m\nu} \right\} f_{m\nu}(z) = \frac{e^2}{\hat{\rho}} \tilde{J}_{m\nu}(z), \end{aligned} \quad (6.10)$$

where

$$\tilde{K}_m(z) \equiv \sum_{m',\nu'} \sigma_{m'\nu'} \int \tilde{D}_{mm'}(z-z') |f_{m'\nu'}(z')|^2 dz', \quad (6.11a)$$

$$\begin{aligned} \tilde{J}_{m\nu}(z) \equiv \sum_{m',\nu'} \sigma_{m'\nu'} f_{m'\nu'}(z) \int \tilde{G}_{m\nu m'\nu'}(z-z') f_{m'\nu'}^*(z') \\ \times f_{m\nu}(z') dz'. \end{aligned} \quad (6.11b)$$

The occupation numbers are determined by the variational equations

$$\epsilon_{F_{m\nu}} \equiv \frac{\partial E}{\partial \sigma_{m\nu}} = \epsilon_F, \quad (6.12)$$

where the Fermi energy  $\epsilon_F$  is the Lagrange multiplier associated with the electron-number constraint

$$\sum_{m,\nu} \sigma_{m\nu} = Z. \quad (6.13)$$

The energy of electrons at the top of the Fermi sea is  $\epsilon_F$ , while that of electrons at the top of the  $m\nu$  band is  $\epsilon_{F_{m\nu}}$ . In our ansatz (Sec. V) the occupation numbers do not exceed 1, so the Fermi energy of fully occupied orbitals ( $\sigma_{m\nu} = 1$ ) is below  $\epsilon_F$ .

The maximum energy in a band is higher than the minimum energy of that band,

$$\epsilon_{F_{m\nu}} > \epsilon_{m\nu}, \quad (6.14)$$

the difference being in the kinetic energy and the exchange kernels. From (6.9c) and (6.12), the Fermi exchange kernel is

$$\begin{aligned} \tilde{G}_{F_{m\nu m'\nu'}}(z) = & \sum_{n=-\infty}^{\infty} \cos(\sigma_{m\nu} z_n \pi / a) \frac{\sin(\sigma_{m'\nu'} z_n \pi / a)}{\sigma_{m\nu} z_n \pi / a} \\ & \times G_{mm'}(z_n). \end{aligned} \quad (6.15)$$

We determine the occupation numbers by iteration. We separate the single-particle Fermi energy into the plane-wave kinetic energy term and the remainder:

$$\begin{aligned} \epsilon_{F_{m\nu}} = & \frac{\hbar^2}{2M} \left[ \frac{\sigma_{m\nu} \pi}{a} \right]^2 \\ & + \left[ \frac{\hbar^2}{2M} \int |f'_{m\nu}(z)|^2 + \frac{\partial E_{en}}{\partial \sigma_{m\nu}} + \frac{\partial E_{ee}}{\partial \sigma_{m\nu}} \right]. \end{aligned} \quad (6.16)$$

During each iteration of the wave functions (Sec. IV), we calculate the remainder in (6.16) using the old occupation numbers and then find by subiteration the new occupation numbers that solve (6.12), (6.13), and (6.16).

The chain equations generalize the isolated-atom equations (the latter are a special case,  $a = \infty$ ). The integro-differential equations for the wave functions are solved similarly, except for some technical complications that occur for finite spacing, as we now discuss.

The large cell  $[-l, l]$  defining the  $z$  coordinate is replaced by the unit cell  $[-a/2, a/2]$  and the boundary conditions are replaced by

$$f'_{m\nu} \left[ \frac{a}{2} \right] = 0, \quad \nu \text{ even} \quad (6.17a)$$

$$f_{m\nu} \left[ \frac{a}{2} \right] = 0, \quad \nu \text{ odd}. \quad (6.17b)$$

The summation over cells is best handled by Fourier transform. For a periodic kernel of the form (6.9),

$$\tilde{h}(z) = \sum_n h(z_n), \quad (6.18)$$

the transform is simply

$$\tilde{h}(q) = \int_{z=-Na/2}^{Na/2} e^{iqz} h(z) dz \rightarrow h(q), \quad (6.19)$$

with the exception of  $q=0$ , where the integral diverges. This transformation to Fourier space isolates the diver-

gence in the  $q=0$  part, and eliminates the dependence of the divergence on the wave function:

$$\begin{aligned} \int V(z) |f(z)|^2 dz = & \frac{1}{a} \sum_{n(\neq 0)} \int V(q_n) |f(z)|^2 e^{-iq_n z} dz \\ & + \frac{1}{a} V(q=0), \end{aligned} \quad (6.20)$$

with a similar expression for the direct kernel. Here  $q_n = 2\pi n/a$ . The Fourier sum converges rapidly, but the sum of the divergent terms must be done before the limit  $N \rightarrow \infty$  is taken.

For the nucleus-electron interaction, the  $q=0$  part is

$$\begin{aligned} E_{eZ}(q=0) = & -\frac{Ze^2}{a\hat{\rho}} \sum_{m,\nu} \sigma_{m\nu} \int_{-a/2}^{a/2} \tilde{V}_m(q=0) |f_{m\nu}|^2 dz \\ = & -\frac{Ze^2}{a\hat{\rho}} \sum_{m,\nu} \sigma_{m\nu} F_{m\nu} \int_{-Na/2}^{Na/2} V_m(z') dz', \end{aligned} \quad (6.21)$$

where

$$F_{m\nu} = \int_{-a/2}^{a/2} |f_{m\nu}(z)|^2 dz = 1. \quad (6.22)$$

Note that  $F_{m\nu}$  must be included explicitly as it contributes to  $\delta E / \delta f_{m\nu}(z)$  and therefore to  $\epsilon_{m\nu}$ . However, we will occasionally omit it from the equations for brevity. From the representation of the nuclear kernel (4.3), we evaluate the integral. For large  $N$ ,

$$\begin{aligned} \int_{-Na/2}^{Na/2} V_m(z') dz' = & \frac{2}{m!} \int_0^\infty e^{-y} y^m dy \int_0^{Na/2} \frac{dz}{\sqrt{2y+z^2}} \\ \rightarrow & \frac{2}{m!} \int_0^\infty e^{-y} y^m \ln \left[ \frac{Na}{\sqrt{2y}} \right] dy \\ = & 2 \ln(Na) - \psi(m+1), \end{aligned} \quad (6.23)$$

where  $y \equiv \rho^2/2$ , and  $\psi(m)$  is the logarithmic derivative of the  $\Gamma$  function. The last two equations imply that

$$E_{eZ}(q=0) = -\frac{2e^2 Z^2}{a\hat{\rho}} \left[ \ln(Na) - \frac{1}{2Z} \sum_{m,\nu} \sigma_{m\nu} \psi(m+1) \right]. \quad (6.24)$$

The  $q=0$  part of the direct interaction is evaluated similarly:

$$\begin{aligned} E_{ee}(q=0) = & \frac{e^2}{a\hat{\rho}} \sum_{m,\nu,m',\nu'} \sigma_{m\nu} \sigma_{m'\nu'} \int_{-a/2}^{a/2} \tilde{D}_{mm'}(q=0) |f_{m\nu}(z)|^2 dz |f_{m'\nu'}(z')|^2 dz' \\ = & \frac{e^2}{a\hat{\rho}} \sum_{m,\nu,m',\nu'} \sigma_{m\nu} \sigma_{m'\nu'} F_{m\nu} F_{m'\nu'} \sum_l d_l(m, m') V_l(q=0) \\ = & \frac{e^2 Z^2}{a\hat{\rho}} \left[ \ln \left[ \frac{Na}{2} \right] - \frac{1}{2Z^2} \sum_{m,\nu,m',\nu'} \sigma_{m\nu} \sigma_{m'\nu'} Y_{mm'} \right], \end{aligned} \quad (6.25)$$



where

$$Y_{mm'} \equiv \sum_l^{m+m'} d_l(m, m') \psi(l+1), \quad (6.26)$$

and we used both the expansion (4.12) and the sum rule for the  $d$  coefficients

$$\sum_l d_l(m, m') = 1, \quad (6.27)$$

which is a special case ( $y=0$ ) of the definition (4.11).

The internucleus repulsion also contains a divergent term independent of the electronic wave functions, so that we must add to the  $q=0$  part of the energy

$$E_{ZZ} = \frac{Z^2}{a\hat{\rho}} \sum_{j=1}^{N/2} \frac{1}{j} \rightarrow \frac{Z^2}{a\hat{\rho}} \left[ \ln \left[ \frac{N}{2} \right] + \gamma \right], \quad (6.28)$$

where  $\gamma$  is the Euler constant, 0.577. . . .

The finite sum of the divergent terms [Eqs. (5.24), (5.25), and (5.28)] is

$$E(q=0) = \frac{Z^2 e^2}{a\hat{\rho}} \left[ -\ln(2a) + \gamma + \frac{1}{Z} \sum_{m,v} \sigma_{m,v} \psi(m+1) - \frac{1}{2Z^2} \sum_{m,m'} \sigma_{mm'} Y_{mm'} \right], \quad (6.29)$$

which is the total potential energy of a chain of electrons that are distributed uniformly along the  $z$  axis [ $f_{m,v}(z) = \text{const}$ ]. Numerical comparisons show that this expression agrees with the expression that Refs. 10 and 18 obtained by a different method.

A careful inclusion of the  $F_{m,v}$  factors shows that the  $q=0$  contribution to the single-particle energies is

$$\epsilon_{m,v} = \epsilon_{m,v}(q \neq 0) + \frac{Ze^2}{a\hat{\rho}} \left[ -2 \ln(2) + \psi(m+1) - \frac{1}{Z} \sum_{m',v'} \sigma_{m',v'} Y_{mm'} \right], \quad (6.30)$$

with an identical contribution to the Fermi energy.

The Bloch factor modifies the Fourier transform of the exchange kernels:

$$\tilde{G}_{mvm'v'}(q) = \frac{1}{2\pi} \int B(q') G_{mm'}(q-q') dq', \quad (6.31)$$

where we introduced the Bloch factor  $B(z)$ ,

$$B(z) = \frac{\sin(\sigma_{m,v} z \pi / a)}{\sigma_{m,v} z \pi / a} \frac{\sigma(\sigma_{m',v'} z \pi / a)}{\sigma_{m',v'} z \pi / a}, \quad (6.32)$$

and its Fourier transform  $B(q)$ ,

$$B(q) = \begin{cases} a \sigma_{m,v} & a |q| / \pi < (\sigma_{m,v} - \sigma_{m',v'}) \\ a(\sigma_{m,v} + \sigma_{m',v'} - a |q| / \pi), & (\sigma_{m,v} - \sigma_{m',v'}) < a |q| / \pi < (\sigma_{m,v} + \sigma_{m',v'}) \\ 0, & (\sigma_{m,v} + \sigma_{m',v'}) < a |q| / \pi. \end{cases} \quad (6.33)$$

With no loss of generality, we assume  $\sigma_{m,v} > \sigma_{m',v'}$ . The modified kernel thus can be written in the form

$$\tilde{G}_{mvm'v'} = \sum_l g_l(m, m') \left[ \alpha \int V_l(q') dq' + \beta \int V_l(q') q' dq' \right], \quad (6.34)$$

where the coefficients ( $\alpha, \beta$ ) and the integration limits are functions of  $q$ ,  $\sigma_{m,v}$ , and  $\sigma_{m',v'}$  that are easily determined from (6.33). In our numerical work, we first calculate the integrals

$$\int_0^p V_l(q) dq, \quad \int_0^p q V_l(q) dq \quad (6.35)$$

for a sufficiently fine grid of  $p$ 's. Then, for each set  $\{m, v, m', v', q_n\}$  we determine the integration limits in (6.34) and interpolate the two functions (6.35). We could avoid the interpolation by approximating the dependence of (6.34) on  $\sigma_{m,v}$  by an effective mass. (Although a similar approximation is often used in band structure calculations, we avoided it because the errors it induces in this case are not necessarily small.) The number of  $p$  grid points that are necessary to reach convergence depends upon the internuclear spacing  $a$ ; typically, a few thousand points for each Landau orbital are sufficient.

To reduce computation time, we replace the probability density of the outer orbitals with a constant. The precise balance between the number of  $z$ -dependent and  $z$ -independent wave functions depends on the internuclear spacing. For iron, we found that constant wave functions were good approximations beyond  $m=35$ , at least for internuclear spacings where the outer orbitals are not empty.

The number of fully and partially occupied orbitals increases as the internuclear spacing is decreased and eventually grows beyond our numerical capabilities. However, with the 50 Landau orbitals that we use in our calculations of iron, the energy at the minimum separation is much higher than the isolated-atom energy (by  $\sim 30\%$ , see Sec. VII). This energy is high enough that we can be certain that there is no deep minima at smaller spacings.

## VII. RESULTS

Some of our results first presented in Ref. 6 are repeated here for the reader's convenience. Table I shows our calculated energies of isolated helium, carbon, and iron atoms at two field strengths,  $B_{12}=1$  and  $B_{12}=5$ , together with a comparison to previous calculations, while Table II displays some properties of our iron atom solu-

TABLE I. Absolute values of the ground-state binding energies of atoms calculated in the Hartree-Fock approximation, are compared with density-functional (DF) (Ref. 11), density-functional with correlations (DFC) (Ref. 11), Thomas-Fermi-Dirac (TFD) (Ref. 20), and restricted-variational (RV) (Ref. 10) calculations. Energies are given in keV.

$Z$	$B_{12}$	HF	DF	DFC	TFD	RV
2	1	0.575 32				0.545
	5	0.958	1.040			0.913
6	1	4.230			4.14	
	5	7.668	8.03		7.73	
26	1	55.10	56.1		56.21	53.13
	5	106.09	108.18	108.85	105.89	101.7

tion. Our results for helium agree with those of Ref. 7 to five significant digits. We also note that for iron at  $B_{12}=5$ , a combination of the Hartree energy (Ref. 11) with the exchange energy from variational calculations yields an approximate Hartree-Fock energy  $-106.18$  keV (Ref. 11), in agreement with our result,  $-106.09$  keV. Our binding energies are slightly less than those from the density-functional calculations. As explained in Sec. III, we attribute this difference to the use of uniform-density exchange functionals in the latter calculations; the Landau orbitals of the present case are well localized in the plane perpendicular to the field, and do not resemble plane waves.

Figure 1 shows the energy per unit cell of a chain as a function of the internuclear spacing. We find that helium is bound in chains, in agreement with Refs. 10 and 11; our binding energies per atom are 25 eV for  $B_{12}=1$  and 150 eV for  $B_{12}=5$ . However, we find that carbon and iron chains are not bound. Repeating our calculations for  $Z=3$  through 5, we find that atoms with  $Z > 2(4)$  are unbound at  $B_{12}=1(5)$ . The shapes of the curves agree approximately with the density-functional results; the differences can again be attributed to the approximate treatment of the exchange interaction in Ref. 11.

For large internuclear spacings, the binding energy of the chain (relative to that of the isolated atom) is dominated by the ( $a^{-2}$ ) repulsion term from the Bloch plane waves. However, as we explained in Sec. VI, for very large spacings the  $e^{ikzf}(z)$  ansatz is not appropriate, and a better ansatz gives an exponentially decreasing kinetic energy. The total energy will therefore be dominated by the  $a^{-5}$  quadrupole-quadrupole attraction, which dominates the interaction energy of two separated atoms.

TABLE II. Ionization and  $K$ -shell energies, and the kinetic, nuclear-electron, direct electron-electron, and exchange contributions to the total energy of an iron atom at  $B_{12}=1,5$ . The energies are given in keV.

$B_{12}$	$E_1$	$E_K$	$\langle H_B \rangle$	$\langle V_{eZ} \rangle$	$\langle V_{ee} \rangle$ direct	$\langle V_{ee} \rangle$ exchange
1	0.12	-7.23	10.6	-95.4	32.7	-3.06
5	0.25	-13.86	19.78	-181.7	61.3	-5.41

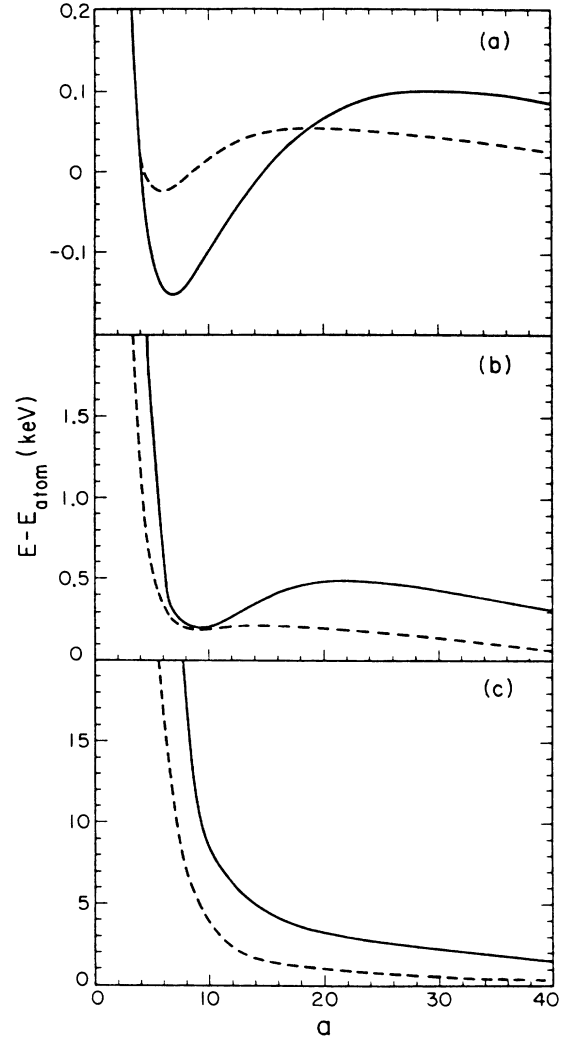


FIG. 1. The ground-state energies per unit cell of infinite linear chains of helium (a), carbon (b), and iron (c) are shown as functions of the internuclear separation for  $B_{12}=1$  (dashed lines) and 5 (solid lines). The energies are relative to the isolated-atom values. The unit length is  $2.566 \times 10^{-10} \text{ cm} \times B_{12}^{-1/2}$ .

The chain-chain interaction may bind matter into chains even if isolated chains are unbound. The cohesive energy is estimated to be smaller than 0.5 keV. However, most physical consequences of such weak binding are similar to those of no binding. For example, matter in the crust of neutron stars has to be bound by at least 3 keV to resist the strong electric field that tries to tear matter from the surface.

TABLE III. The single-particle energies of iron atoms at (a)  $B_{12}=1$  and (b)  $B_{12}=5$ , and their various components: kinetic, nuclear-electron, direct electron-electron, and exchange. The energies are given in keV.

$m$	$\nu$	$\epsilon_{m\nu}$	$\langle H_B \rangle$	$\langle v_{eZ} \rangle$	$\langle v_{ee} \rangle$ direct	$\langle v_{ee} \rangle$ exchange
(a) $B_{12}=1$						
0	0	-7.23	1.79	-12.1	3.45	-0.427
0	1	-1.38	1.78	-5.95	3.06	-0.277
1	0	-3.60	0.810	-7.30	3.28	-0.387
1	1	-0.678	1.01	-4.24	2.79	-0.242
2	0	-2.36	0.535	-5.68	3.14	-0.358
2	1	-0.392	0.677	-3.42	2.57	-0.216
3	0	-1.71	0.399	-4.80	3.02	-0.333
3	1	-0.241	0.481	-2.89	2.36	-0.191
4	0	-1.31	0.317	-4.23	2.91	-0.312
4	1	-0.148	0.347	-2.48	2.15	-0.163
5	0	-1.04	0.262	-3.83	2.81	-0.290
5	1	-0.082	0.244	-2.12	1.92	-0.128
6	0	-0.839	0.227	-3.52	2.72	-0.268
7	0	-0.692	0.197	-3.27	2.64	-0.251
8	0	-0.582	0.171	-3.07	2.56	-0.238
9	0	-0.497	0.151	-2.90	2.48	-0.228
10	0	-0.430	0.134	-2.75	2.40	-0.219
11	0	-0.377	0.119	-2.62	2.33	-0.211
12	0	-0.334	0.107	-2.50	2.27	-0.203
13	0	-0.298	0.096	-2.40	2.20	-0.195
14	0	-0.268	0.088	-2.31	2.14	-0.187
15	0	-0.243	0.080	-2.23	2.08	-0.179
16	0	-0.219	0.073	-2.15	2.03	-0.169
17	0	-0.197	0.066	-2.08	1.97	-0.157
18	0	-0.174	0.059	-2.01	1.92	-0.142
19	0	-0.142	0.052	-1.94	1.86	-0.116
(b) $B_{12}=5$						
0	0	-13.9	4.24	-23.9	6.58	-0.809
0	1	-0.987	2.55	-8.22	5.08	-0.397
1	0	-7.23	2.09	-14.9	6.27	-0.708
1	1	-0.417	1.43	-5.97	4.43	-0.302
2	0	-4.87	1.45	-11.7	6.03	-0.622
3	0	-3.62	1.11	-9.99	5.83	-0.571
4	0	-2.83	0.901	-8.84	5.64	-0.535
5	0	-2.29	0.753	-8.01	5.47	-0.506
6	0	-1.89	0.643	-7.36	5.31	-0.483
7	0	-1.59	0.558	-6.85	5.16	-0.463
8	0	-1.36	0.490	-6.43	5.02	-0.445
9	0	-1.17	0.435	-6.07	4.89	-0.428
10	0	-1.02	0.389	-5.76	4.77	-0.414
11	0	-0.897	0.350	-5.49	4.64	-0.400
12	0	-0.795	0.316	-5.25	4.53	-0.387
13	0	-0.710	0.288	-5.04	4.42	-0.375
14	0	-0.638	0.263	-4.85	4.31	-0.363
15	0	-0.578	0.242	-4.68	4.21	-0.352
16	0	-0.527	0.223	-4.52	4.11	-0.341
17	0	-0.482	0.206	-4.38	4.02	-0.330
18	0	-0.443	0.191	-4.25	3.93	-0.318
19	0	-0.408	0.177	-4.12	3.84	-0.305
20	0	-0.375	0.165	-4.01	3.76	-0.290
21	0	-0.342	0.152	-3.89	3.67	-0.271
22	0	-0.306	0.139	-3.78	3.58	-0.246
23	0	-0.255	0.124	-3.66	3.48	-0.203

TABLE IV. Absolute values of the ground-state energies of all atoms through  $Z=18$  at  $B_{12}=0.1, 0.5, 1,$  and  $5$ . The energies are given in keV. For the heavier atoms, calculations were done only for large fields, where the adiabatic assumption is valid.

$Z$	$B_{12}$	0.1	0.5	1.0	5.0
1		0.0761	0.130	0.161	0.2550
2		0.255	0.454	0.574	0.9580
3		0.516	0.944	1.209	2.0760
4		0.846	1.580	2.042	3.5840
5		1.238	2.347	3.054	5.4560
6		1.678	3.22	4.20	7.60
7		2.17	4.22	5.54	10.20
8		2.71	5.32	7.02	13.00
9		3.36	6.51	8.63	16.10
10			7.819	10.39	19.57
11			9.197	12.25	24.64
12			10.72	14.23	27.17
13			12.32	16.34	31.35
14			14.00	18.60	35.74
15			15.79	20.95	40.35
16			17.67	23.43	45.22
17			19.64	26.07	50.30
18			21.72	28.82	55.95

Our interest in this problem was sparked by the confusion over the results of restricted variational calculations.<sup>10</sup> Originally, these calculations predicted large cohesive energy, but numerical errors were found and the corrected calculations predicted that chains are unbound. However, as Table I shows, even the corrected calculations underestimate the absolute binding energies by 5%, which is more than our cohesive energy.

Table III shows the single-particle energies of isolated iron atoms at  $B_{12}=5$ ; also shown are the different components of the energies: kinetic, nucleus-electron Coulomb attraction, direct electron-electron repulsion, and exchange. Figure 2 shows the single-particle energies and the Fermi energies of helium, oxygen, and iron at  $B_{12}=5$  as functions of the internuclear spacing.

For completeness, Table IV displays the energies of all isolated atoms to  $Z=18$  at various field strengths. As shown in Fig. 3, the energy follows a  $Z^{9/5}B^{2/5}$  dependence, in accordance with theoretical studies.<sup>19</sup> From

TABLE V. The number of occupied one-node orbitals in the ground state of all atoms with  $Z \leq 18$  and of iron, at various field strengths.

$Z \backslash B_{12}$	0.1	0.5	1.0	5.0
1-9	0	0	0	0
10		0	0	0
11		0	0	0
12		1	0	0
13		1	1	0
14		1	1	0
15		2	1	0
16		2	2	0
17		2	2	0
18		3	2	0
26			6	2

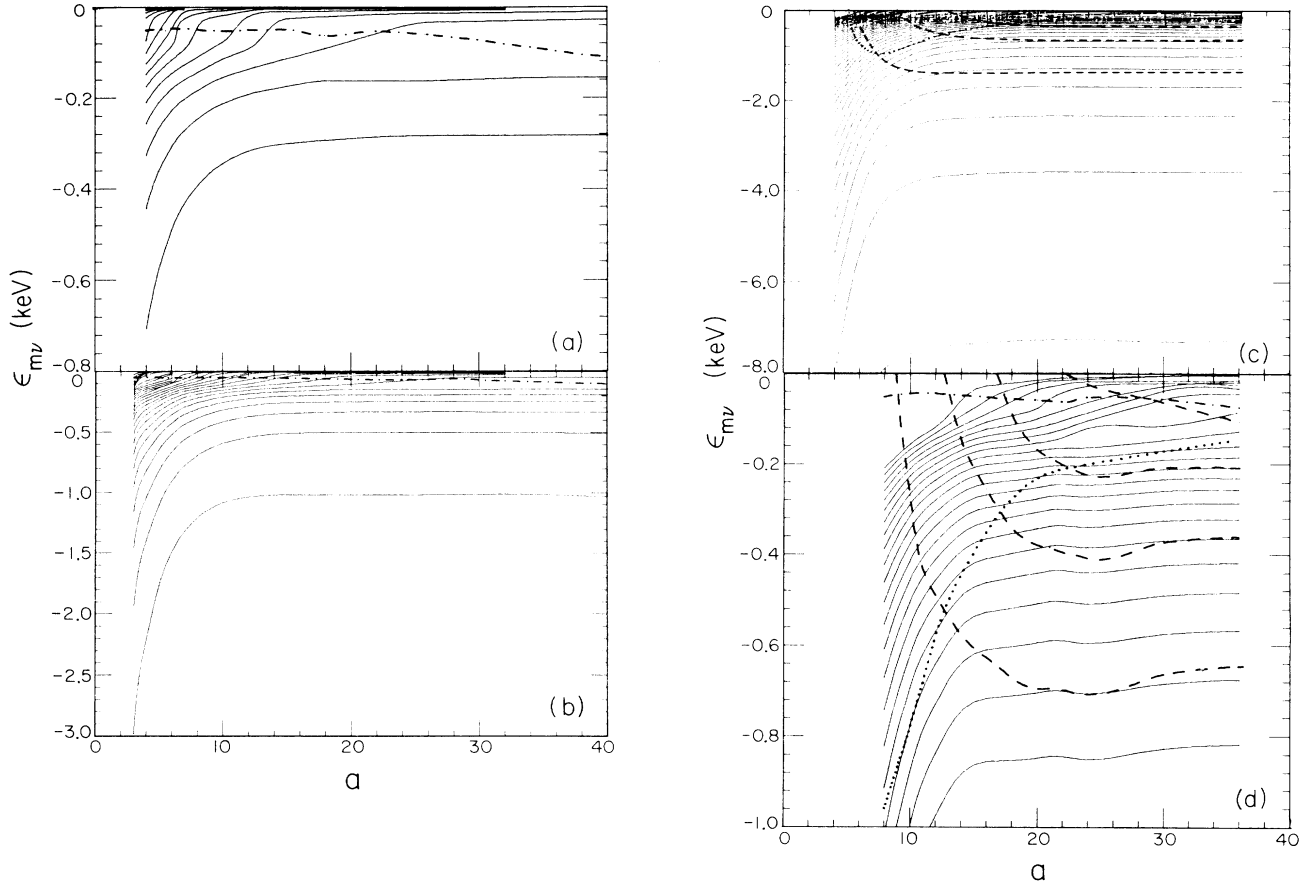


FIG. 2. The Fermi energies (dot-dashed lines) and the single-particle energies of electrons in zero-node states (solid lines), one-node states (dashed lines), and two-node states (dotted lines), for infinite linear chains of helium (a), carbon (b), and iron (c) and (d). The energies are shown as functions of the internuclear separation for all occupied orbitals at  $B_{12}=1$ . Panel (d) is the same as (c), except that it uses a finer scale, to show clearly the energies of the upper orbitals. The unit of length is as in Fig. 1.

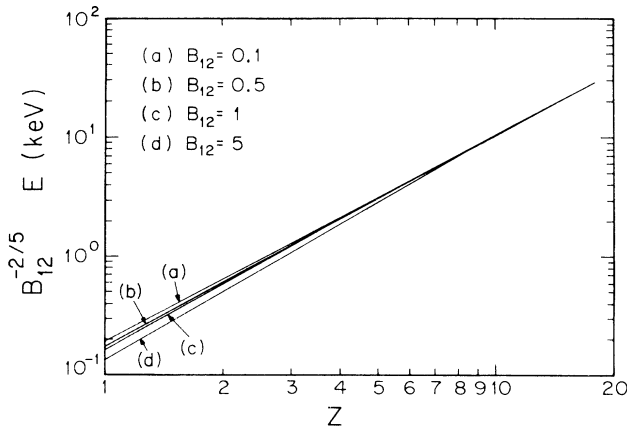


FIG. 3. The binding energies of isolated atoms in strong fields are shown as functions of  $Z$  for  $B_{12}=0.1, 0.5, 1,$  and  $5$ . The energies are scaled by  $B_{12}^{-2/5}$ , and logarithmic scales are used to show clearly the  $Z^{9/5}B_{12}^{2/5}$  dependence.

the figure we derive

$$E \sim -158 \text{ eV} \times Z^{9/5} B_{12}^{2/5}, \quad (7.1)$$

while in Ref. 19 an approximate bound of  $-170 \text{ keV}$  for the coefficient was found. This expression holds for fields that are strong, but not ultrastrong. In Ref. 16 it is shown that when the magnetic field is very large,  $B \geq 2Z^3 B_C$ , the  $B^{2/5}$  dependence is replaced by a logarithmic dependence.

We found that for  $Z \leq 18$  only zero-node ( $\nu=0$ ) and one-node ( $\nu=1$ ) states are occupied. Lists of occupied one-node states for all atoms up to  $Z=18$  and for iron, for various field strengths, are presented in Table V. The calculation breaks down and the Fermi energy increases above zero at very small internuclear spacings, as a result of the finite number of orbitals included in our calculations (Sec. VI).

In conclusion, we find that, within the Hartree-Fock approximation, chains of heavy atoms in strong magnetic fields are unbound. There are, of course, corrections

that could be applied to refine our results: interelectron correlations,  $k$  dependence in the bands, and interchain interactions. We have presented arguments above that any cohesive energy induced by each of these effects are likely to be very small ( $\lesssim 1\%$  or 1 keV for Fe). While

further refinements in the precision of our calculation would perhaps be desirable, they are unnecessary to resolve the nature of the neutron star surfaces, where a cohesive energy of at least 3 keV per Fe atom is required to support a solid.

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