NATURAL ORBITALS IN RELATION TO QUANTUM INFORMATION THEORY: FROM MODEL LIGHT ATOMS THROUGH TO EMERGENT METALLIC PROPERTIES

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The review begins with a consideration of 3 forms of quantum information entropy associated with Shannon and Jaynes. For model two-electron spin compensated systems, some analytic progress is first reported. The Jaynes entropy is clearly related to correlation kinetic energy. A way of testing the usefulness of a known uncertainty principle inequality is proposed for a whole class of model two-electron atoms with harmonic confinement but variable electron-electron interaction.

Emerging properties are then studied by reference to bcc Na at ambient pressure and its modeling by ‘jellium’. Jellium itself has collective behaviour with changes of the density, especially noteworthy being the discontinuity of the momentum distribution at the Fermi surface. This has almost reduced to zero at \( r_s = 100 \) a.u., the neighbourhood in which the quantal Wigner electron solid transition is known to occur. However, various workers have studied crystalline Na under pressure and their results are compared and contrasted. Work by DFT on K, Rb, and Cs is discussed, but now with reduced density from the ambient pressure value. The crystalline results for the cohesive energy of these metals as a function of lattice parameters and local coordination number are shown to

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be closely reproduced by means of ground and excited states for dimer potential energy curves.

Then, pair potentials for liquid Na and Be are reviewed, and compared with the results of computer simulations from the experimental structure factor for Na.

Finally, magnetic field effects are discussed. First a phenomenological model of the metal-to-insulator transition is presented with an order parameter which is the discontinuity in the Fermi momentum distribution. Lastly, experiments on a two-dimensional electron assembly in a GaAs/AlGaAs heterojunction in a perpendicular magnetic field are briefly reviewed and then interpreted.

Keywords: Quantum information entropy; Natural orbitals; Emergent properties; Metal-to-insulator transitions; Alkali metals under pressure

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Appendix A. Relation between three forms of quantum information entropy for a whole class of two-electron spin-compensated models
1. Background and outline

The starting point of the present review is the work of Amovilli and March. These authors drew attention to the importance of natural orbitals (NOs) in quantum information theory. These NOs will be defined in Section 2 below, together with a brief summary of some of their properties. But they are still somewhat difficult to obtain, and even in light atoms like He and Be, one must then have recourse to numerical methods. Therefore, in Section 2.1 known explicit analytic forms of NOs for light model atoms will be used to gain insight. Section 3 follows Amovilli and March in expressing quantum information entropy in terms of NO properties.

We then turn for the remainder of this review to emergent properties, with emphasis placed on metallic states. We shall essentially deal with periodic crystalline Na and Be, with the former modelled, at atmospheric pressure, by the Sommerfeld, or as now commonly described ‘jellium’, model. Thus, in metallic bcc Na, the monovalent ionic charges are smeared out into a uniform background of positive charges, neutralizing the interacting electron assembly. A considerable merit of this jellium model is that the NOs are plane waves $e^{ik \cdot r}$; an enormous simplification. However, other properties, including the ground-state energy per electron, are still only known numerically from quantum Monte Carlo simulations, starting with the pioneering work of Ceperley and Alder.

Turning to both Na and Be metals without smearing the ions, we note in Section 4.1 for the benefit of the reader a proof that the NOs have Bloch wave form, $e^{ik \cdot r} u_k(r)$, where $u_k(r)$ is a periodic function with the period of the lattice. Section 5 then contains a discussion of the remarkable effect of applying high pressure to the alkali metals Li, Na, and K. Section 6 treats Be liquid metal in some detail. A phenomenological model of a metal-to-insulator transition in then summarized in Section 7. Because of key experiments using an GaAs/AlGaAs heterojunction in a magnetic field, a summary of such experiments plus some theoretical work is given in Section 8. The final section constitutes a summary, plus some proposals for future research, both theoretical and experimental, that should be fruitful.

2. Definition of natural orbitals (NOs) and calculation for a model of He-like atomic ions

Following Löwdin, we first use the exact (normalized) ground state wave function $\Psi$ for an $N$-electron assembly to define a so-called first-order density matrix $\gamma(r', r)$ by

$$\gamma(r', r) = N \int \Psi^*(r', r_2, \ldots, r_N) \Psi(r, r_2, \ldots, r_N) dr_2 \cdots dr_N. \quad (2.1)$$
This leads to the ground-state density $\rho(r)$, the central tool of DFT\textsuperscript{[5]}, as
\[
\rho(r) = \gamma(r',r)|_{r'=r}. \tag{2.2}
\]
But Löwdin's proposal was to define (normalized) natural orbitals $\phi_i(r)$ and their occupation numbers $n_i$ which bring $\gamma(r',r)$ into the diagonal form
\[
\gamma(r',r) = \sum_i n_i \phi_i^*(r')\phi_i(r). \tag{2.3}
\]
The remainder of this Section will give illustrative examples, for admittedly simplistic models, of the occupation numbers $n_i$ and the orbitals $\phi_i(r)$.

2.1. Explicit forms of NOs for light model atoms, and construction of the first-order density matrix (1DM)

As an example of the (albeit approximate) calculation of NOs and their occupation numbers, we shall consider, following Amovilli, Howard, and March (AHM)\textsuperscript{[6,7,8]} a change in the Hamiltonian $H_T$ proposed long ago by Temkin\textsuperscript{[9]} (see also Ref.\textsuperscript{[10]}).

$H_T$ was obtained from the exact non-relativistic Hamiltonian for He-like atomic ions by replacing the electron-electron interaction $u(r_{12}) = e^2/r_{12}$, where $r_{12} = |r_1 - r_2|$ denotes the relative coordinate of the two electrons, by its spherical average, which becomes then solely $u(r_1, r_2)$, with no longer dependence on the angle between $r_1$ and $r_2$. The Hamiltonian $H_{AHM}$ was then taken to be defined by
\[
H_{AHM} = H_T + \delta(r_1 - r_2), \tag{2.4}
\]
where the $\delta$ function represents an additional radial correlation in an admittedly simplistic manner. AHM\textsuperscript{[6,7,8]} solve this Hamiltonian exactly for non-relativistic He positive ions with external potential
\[
V_{\text{ext}}(r) = -\frac{Ze^2}{r}. \tag{2.5}
\]
This being, of course, already present in $H_T$. Here, we shall focus on their study of the NOs for this Hamiltonian, Eq.\textsuperscript{[2.4]}. If $\Psi$ denotes the symmetric ground-state wave function, the NOs diagonalize the density matrix kernel operator
\[
\gamma(r,r') = 4\pi \int_0^{\infty} dr_2 r_2^2 \Psi(r,r_2)\Psi(r_2,r'). \tag{2.6}
\]
Therefore, by spectral decomposition, we can write
\[
\gamma(r,r') = \sum_j n_j \phi_j(r)\phi_j(r'), \tag{2.7}
\]
where $\sum_j n_j = 1$. Since we have just two electrons, the form\textsuperscript{[2.6]} allows one to write
\[
\Psi(r_1, r_2) = \sum_j \nu_j \phi_j(r_1)\phi_j(r_2), \tag{2.8}
\]
Table 1. First 10 occupation numbers and eigenvalues of the spectral decomposition of the ground-state wave function for He in the modified Temkin $s$-wave model. After Ref. 7.

| $j$ | $\nu_j$ | $n_j$ |
|-----|----------|-------|
| 1   | 0.97856  | 0.95758 |
| 2   | -0.19988 | 0.03995 |
| 3   | -0.04333 | 0.00188 |
| 4   | -0.01911 | 0.00037 |
| 5   | -0.01079 | 0.00012 |
| 6   | -0.00694 | 0.00005 |
| 7   | -0.00484 | 0.00002 |
| 8   | -0.00358 | 0.00001 |
| 9   | -0.00275 | 0.00001 |
| 10  | -0.00218 | 0.00000 |

with $\nu_j^2 = n_j$ and

$$4\pi \int_0^\infty dr_2 r_2^2 \Psi(r_1, r_2) \phi_j(r_2) = \nu_j \phi_j(r_1). \quad (2.9)$$

As Amovilli and March (AM) 7 show, the eigenvalue sum $\sum_j \nu_j$ can also be found. Taking the wave function at coincidence ($r_1 = r_2$), after integration one finds

$$\sum_j \nu_j = \frac{8\pi N}{(2Z - 1)^3}$$

$$= \frac{8(Z - 1)}{2Z - 1} \sqrt{\frac{2Z^2 - 3Z + 1}{32Z^3 - 50Z + 20}}$$

$$= 1 - \frac{15}{32} \frac{1}{Z} + O \left( \frac{1}{Z^2} \right), \quad (2.10)$$

the last expansion applying in the limit of large $Z$. AM 7 then obtain a set of approximate NOs. The first 10 occupation numbers and the corresponding eigenvalues $\nu_j$ as obtained by AM are reproduced in Table 1.

### 2.2. Differential equation for NOs of AHM Hamiltonian

The integral equation (2.9) can, as AM have shown, 7 be transformed into a second-order linear differential equation satisfied by the NOs $\phi_i$. Thus AM find first the integral equation

$$e^{r_1} \int_0^{r_1} dr_2 r_2^2 e^{-Zr_2} \phi_j(r_2) + \int_{r_1}^{\infty} dr_2 r_2^2 e^{-(Z-1)r_2} \phi_j(r_2) = \frac{\nu_j}{4\pi N} e^{Zr_1} \phi_j(r_1). \quad (2.11)$$

Dividing through $e^{r_1}$ and differentiating again, the above equation reduces to a homogeneous second-order linear differential equation for $\phi_j$. After some modest
Manipulation, AM show that the result reads
\[
\phi_j'' + (2Z - 1)\phi_j' + \left(Z(Z - 1) - \frac{4\pi Nr^2}{\nu_j} e^{-(2Z-1)r}\right)\phi_j = 0.
\] (2.12)

This equation is what must be hoped is a forerunner of a corresponding equation of realistic rather than model He-like ions. Eq. (2.12) possesses solutions for any value of \(\nu_j \in [-1, 1]\) apart from \(\nu_j = 0\), with behaviour at small and large \(r\) as listed below
\[
\phi_j \to \exp(-Zr), \quad r \to 0, \quad (2.13a)
\]
\[
\phi_j \to \exp(-(Z - 1)r), \quad r \to \infty. \quad (2.13b)
\]

For further details on \(\nu_j\) and \(n_j\), the interested reader must consult Ref. [7].

A proposed characterization of the correlated 1DM for the ground-state of the Hookean model for a two-electron atom can be found in Ref. [11].

3. Quantum information entropy and NO properties

In most books on DFT, formulae are written for quantum entropy \(S\), in suitable units, in terms of the ground-state density \(\rho(r)\), \(S_\rho\), say, or alternatively the corresponding momentum density \(n(p)\), say \(S_n\). These read
\[
S_\rho = \text{const} \times \int \rho(r) \ln \rho(r) dr
\] (3.1a)
and
\[
S_n = \text{const} \times \int n(p) \ln n(p) dp.
\] (3.1b)

Of course, to be truly interesting, \(S_\rho\) and \(S_n\) should be calculated from fully correlated ground-state densities in both \(r\) and \(p\) space. Such densities are now obviously available in numerical form only, however, using well-known quantum-chemical techniques like the coupled-cluster method.

In fact, as Amovilli and March [10] pointed out, a quantity known also to information theory workers, the so-called Jaynes entropy, and related to the correlated 1DM \(\gamma(r', r)\), could be evaluated solely in terms of occupation numbers \(n_i\) introduced in Section 2 above. The Löwdin natural orbitals \(\phi_i(r)\) are not required, the result for an \(N\)-electron system being [11]
\[
S_{\text{Jaynes}} = \text{const} \times \sum_i \frac{n_i}{N} \ln \left(\frac{n_i}{N}\right). \quad (3.2)
\]

As a more recent example than those cited in Section 2.1, it is relevant here to mention the model studied by Schilling et al. [12]. For spinless Fermions in one dimension, these authors studied a generalized Moshinsky Hamiltonian (see Ref. [13] and references therein), namely
\[
H = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + \frac{1}{2}m\omega^2x_i^2\right) + \frac{1}{2}D \sum_{i,j=1}^{N} (x_i - x_j)^2. \quad (3.3)
\]
Natural lengths they single out are identified by
\[ \ell = \sqrt{\frac{\hbar}{m\omega}}, \]  
\[ \tilde{\ell} = \sqrt{\frac{\hbar}{m\omega\sqrt{1 + ND/m\omega^2}}}, \]
for \( N \) identical Fermions. They in fact parametrize the coupling by writing
\[ \delta = \ln \left( \frac{\ell}{\tilde{\ell}} \right) = \frac{1}{4} \ln \left( 1 + \frac{ND}{m\omega^2} \right). \]  
They obtain then the exact correlated 1DM as
\[ \gamma(x', x) = p(x', x) \exp \left( -\alpha(x'^2 + x^2) + \beta x' x \right), \]
where \( p \) denotes a symmetric polynomial of degree \( 2(N-1) \) in the variables \( x' \) and \( x \), while \( \alpha \) and \( \beta \) are constants depending on \( \ell, \tilde{\ell}, \) and \( N \).

To summarize their achievement concerning the occupation number \( n_i \), they note a duality property
\[ n_i(\delta) = n_i(-\delta) \]  
relating attractive (\( \delta < 0 \)) and repulsive (\( \delta > 0 \)) Fermion-Fermion interactions. This means that expansions of \( n_i \) in powers of \( \delta \) contain only even order terms. Schilling et al.\(^{12}\) give the first eight occupation numbers to \( O(\delta^{10}) \), for the case \( N = 3 \). So, at least in this admittedly simplistic example, the Jaynes entropy via Eq. \((3.2)\) can be estimated.

4. Emergent properties, especially to metallic states
4.1. NOs of periodic crystal: proof that they have Bloch wave form

As we consider crystalline properties, it is of obvious interest to enquire what is the nature of the NOs in such assemblies (see also Ref. \(^{14}\)). Let us expand the ground-state wave function \( \Psi \) in products of single-particle orthonormal functions as
\[ \Psi = \sum_{\ell_1, \ldots, \ell_N} c(\ell_1, \ldots, \ell_N) \phi_{\ell_1}(r_1) \cdots \phi_{\ell_N}(r_N), \]  
where \( N \) is the number of electrons. Note that the coefficients must be chosen to take care of Fermion antisymmetry. We may write for the 1DM that
\[ \gamma(r', r) = \sum_{k\ell} \alpha_{k\ell} \phi_k(r')^* \phi_\ell(r), \]  
where
\[ \alpha_{k\ell} = N \sum_{\ell_1, \ldots, \ell_N} c^*(k, \ell_2, \ldots, \ell_N) c(\ell, \ell_2, \ldots, \ell_N). \]
Since the $\alpha_{k\ell}$ form an Hermitean matrix, it can therefore be brought into diagonal form. Let $b_{\ell m}$ the elements of the diagonalizing matrix. Next define the orthonormal set

$$\psi_{\ell} = \sum_m b_{\ell m} \phi_m.$$  
(4.4)

Eq. (4.2) then becomes

$$\gamma(r',r) = \sum_{\ell} a_{\ell} \psi_{\ell}^*(r') \psi_{\ell}(r),$$  
(4.5)

as discussed earlier in this Review. The orbitals $\psi_{\ell}$ are the NOs and the $a_{\ell}$ are occupation numbers.

Here, it is to be noted that, if $\Psi$ is normalized to unity, then

$$\sum_{\ell_1, \ldots, \ell_N} |c(\ell_1, \ldots, \ell_N)|^2 = 1 \quad (4.6a)$$

and

$$\sum_i a_i = N, \quad (4.6b)$$

It is further to be noted that the coefficients $c(\ell_1, \ldots, \ell_N)$ are antisymmetric in $\ell_1, \ldots, \ell_N$, since $\Psi$ is an antisymmetric wave function. This implies that one can write

$$\Psi = \sum_K c_K \Psi_K,$$  
(4.7)

where $K$ denotes a ‘configuration’ $\ell_1 < \ell_2 < \ldots < \ell_N$, while $\Psi_K$ is a normalized determinant

$$\Psi_K = \left( \frac{1}{N!} \right)^{1/2} \det \psi_i(r_j).$$  
(4.8)

It is readily shown that $c_K = (N!)^{1/2} c(\ell_1, \ldots, \ell_N)$ and

$$\sum_K |c_K|^2 = 1. \quad (4.9)$$

In the Hartree-Fock (HF) approximation, $\Psi$ is a single determinant having the form (4.8) above, and the $a_\ell$ of Eq. (4.5) are either zero or unity. Generalizing this, it can be shown that

$$a_\ell = \sum_{K(\ell)} |c_K|^2,$$  
(4.10)

the sum extending over all configurations including $\ell$. But because of Eq. (4.9), it follows that

$$0 \leq a_\ell \leq 1 \quad \text{all } \ell. \quad (4.11)$$

This summarizes the so-called Pauli conditions on the 1DM.
This is the stage to show that, for an ideal crystal, the NOs must have Bloch function form. That is, they are such that
\[ \psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_\mu) = e^{i\mathbf{k} \cdot \mathbf{R}_\mu} \psi_{\mathbf{k}}(\mathbf{r}), \]
for all vectors \( \mathbf{R}_\mu \) in the Bravais lattice. To prove this, it is to be noted that, taking periodic boundary conditions,
\[ |\Psi(\mathbf{r}_1 + \mathbf{R}_\mu, \ldots, \mathbf{r}_N + \mathbf{R}_\mu)|^2 = |\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2, \]
which merely expresses the physical equivalence of every cell in a perfect crystal. From the above equation, it follows that
\[ \Psi(\mathbf{r}_1 + \mathbf{R}_\mu, \ldots, \mathbf{r}_N + \mathbf{R}_\mu) = \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \exp(i\mathbf{K} \cdot \mathbf{R}_\mu). \]
Next one can expand in orthogonal Bloch functions \( \phi_{\ell\mathbf{k}} \), where \( \ell \) denotes an index corresponding to the band index of the independent particle model:
\[ \Psi = \sum_{\ell k} \alpha_{\ell k} \phi_{\ell k}(\mathbf{r}_1) \cdots \phi_{\ell N k_N}(\mathbf{r}_N). \]
It is easy to show that the sum over the \( k \)'s is restricted by the condition
\[ \sum_{i=1}^{N} k_i = \mathbf{K}, \]
so that one may write
\[ \gamma(\mathbf{r}, \mathbf{r}') = \sum_{\ell m k} \alpha_{\ell m}(\mathbf{k}) \phi_{\ell k}(\mathbf{r}') \phi_{m k}(\mathbf{r}). \]
Thus, for a set of Bloch wave functions, the occupation numbers are always diagonal in \( k \).

It remains to diagonalize in the ‘band’ indices \( \ell \) and \( m \). The diagonalizing matrix \( b_{\ell m} \) is dependent on \( k \), but being unitary, the NOs
\[ \psi_{\ell k}(\mathbf{r}) = \sum_{m} b_{\ell m}(\mathbf{k}) \phi_{m k}(\mathbf{r}) \]
obey condition (4.12) since the \( \phi_{m k} \) do so. As a special case, the NOs of homogeneous jellium must be plane waves: a fact we have already utilized in an earlier section.

5. Li, Na, and K under pressure

5.1. Alkali metals under extreme conditions, especially Li and Na

Because of their relatively simple electronic structure and relatively high electron density, light alkali metals in normal conditions, including Li, Na, and K, have long been considered to have a ‘simple’ metallic behaviour. The free-electron model was also believed to work even better at higher pressure and electron density. Such a ‘tenet’ was first reconsidered by Siringo et al., who, already in the title of their work, explicitly posed the question whether the light alkali metals are still metals...
under high pressure. These authors studied an extended Hubbard model on a bcc lattice, characterized by an on-site electron repulsion $U$ and an intersite electron interaction $V$. The main result of their work was that such a model electron system should undergo a metal-to-insulator transition with increasing electron density. Such a transition occurred at a critical value of the adimensional Wigner-Seitz radius of $r_s = 2.6$, corresponding to a pressure $p = 100$ GPa for Na. Later works by the same authors even predicted re-entrant metallicity at yet higher pressure, corresponding to oscillations between a symmetric (metallic) phase and a low-symmetry (dimerized and insulating) phase, as a consequence of Friedel oscillations in the electron pair potential $^{17,18}$.

The original finding by Siringo et al. $^{16}$ was followed by DFT studies on dense lithium by Neaton and Ashcroft $^{19}$, who predicted a structural instability of bcc Li towards a more complex Cmca structure at high pressure. In this structure, each Li ion is coordinated by another ion only, and the pairing thereof can give rise to a metal-to-insulator transition at some $r_s < 2.1$. According to Neaton and Ashcroft $^{19}$, the initial distortion is due to the Jahn-Teller mechanism, while further distortion is due to a balance between the Peierls instability and exchange effects.

The above theoretical findings immediately kindled much experimental interest $^{20,21,22}$, which confirmed the tendency of the light alkali metals to lower their symmetry under high pressure. Low symmetry phases have been indeed observed for Li $^{21}$ and Na $^{23,24}$. In particular for Li, Hanfland et al. $^{21}$ established experimentally and theoretically that a cI16 structure stabilizes at $p \approx 40$ GPa and $T \approx 180$ K. The existence of a broken symmetry phase was confirmed by the observation of Goncharov et al. $^{25}$ of a Raman vibrational band in Li above 70 GPa to 120 GPa, the thus confirming the theoretical prediction by Matsuoka et al. $^{26}$ and by Struzhkin et al. $^{27}$ of the existence of two further phases of Li, viz. Li-VI and Li-VII, which are stable at $T = 25$ K and $p = 69$ GPa and $p = 86$ GPa, respectively. Furthermore, Matsuoka and Shimizu $^{28}$, by performing electrical measurements up to 105 GPa, have inequivocally found that a metal-to-insulator transition occurs in Li near 80 GPa at $T < 50$ K. Preliminary calculations $^{29}$ seemed to indicate that both Li and Na show a tendency towards the formation of atomic pairs, and a dimerized oC8 structure was predicted to be the most stable phase above 165 GPa for Li, and above 220 GPa for Na. According to more recent and compelling calculations, several proposals have been made for the identification of the structures of the Li-VI and Li-VII phases, including the oC88 and oC40 structures $^{30}$, the c2-24 and Aba2-24 structures $^{31}$, and more recently an Aba2-40 structure $^{32,33}$.

Analogies and differences between Li and Na under pressure have been described in detail by Rousseau et al. $^{34}$. Like Li, Na crystallizes in the bcc structure at ambient conditions, and undergoes a structural transition towards the fcc phase at 65 GPa $^{35}$. Increasing pressure up to $p = 103$ GPa, Na takes the Na-III phase $^{24,36}$, which has a cI16 symmetry, which is similar to the symmetry adopted by compressed Li. However, above $p = 117$ GPa, the Na-III phase tranforms into the Na-IV phase $^{30,37}$, which is characterized by an oP8 symmetry. Yet two more phases
of Na have been discovered, viz. Na-V above $p = 125$ GPa (Refs. 36,37), and Na-VI above $p = 200$ GPa (Ref. 38). This latter phase presents a simple double-hexagonal close-packed (dhcp) structure, with hP4 symmetry, and is typically transparent 38. The hP4 structure has been confirmed also theoretically by Gatti et al. 39.

The physical reason for dimerization is an open question. Ab initio electronic structure calculations 40 indicated a tendency towards distance alternation, due to a sizeable overlap of $p\pi$ orbitals in the interstitial regions, and to electron localization between ions 41,42. On the other hand, it has been proposed 29,43 that the increase of $s$-$p$ hybridization could give rise to a low coordination number. However, even the fully dimerized phase is far from any standard covalent solid: the electron density is uniformly spread and almost constant, while the first and second neighbours distances are comparable. Such a dimerized phase is better described as a charge density wave in a high density metal rather than a molecular solid. Such a low-symmetry phase in distorted cubic-based structures, as those observed experimentally in the compressed alkalis, has been connected by Angilella et al. 17,18 to the presence of Friedel oscillations in the electronic pair potential. These can ultimately be traced back to the existence of a sharp Fermi surface, and should therefore be generic to most metals.

The deceivingly ‘simple’ light alkali metals are a continuous source of experimental surprises and theoretical challenges. Recently, earlier predictions of superconductivity in compressed lithium 44 have been confirmed experimentally 45,27,46,26. At variance with Li, the superconducting critical temperature $T_c$ of Na is predicted to be rather small ($T_c < 1$ K) also in fcc phase 47,48. If constrained in structures with reduced dimensionality (thin layers or wires), both lithium and sodium have been predicted to exhibit other electronic instabilities, such as a ferromagnetic one 49,50. Closer looks at the phase diagram of both lithium and sodium at high pressure indicate that these light alkali metals should rather prefer the liquid state, with lithium being thus the elemental metal with the lowest melting point 51,36,30,52,53,35. Several theoretical works have also been performed both on Li and on Na 55,56,57,58,59,60. Further ab initio calculations at yet higher pressure indicate more complicated crystal structures, a tendency towards a metal-to-semiconducting transition, and the increasingly relevant role of core orbitals in establishing the electronic behaviour of the compressed alkalis. However, both for lithium 28 and sodium 38 a metal-to-insulator transition at high pressure has now been experimentally well established.

5.2. Mainly expanded potassium related to dimer potential energy curves

Relatively early work on potassium subjected to high pressure was carried out by March and Rubio 64. These authors utilized DFT ground-state theory in the local density approximation (LDA).

A variety of different crystal structures were studied in the above work, the
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Fig. 1. Cohesive energy for K lattices corresponding to coordination numbers $z = 8$ (bcc), 4 (diamond), and 2 (chain) as a function of the nearest-neighbour bond length, from \textit{ab initio} calculations. Redrawn after Ref. 64.

bcc structure at atmospheric pressure, with coordination number $z = 8$, being the natural starting point. Of course, the appropriate free energies are all fairly close, so that the intersections showing phase transitions due to change in $z$ are, no doubt, sensitive to the approximation (LDA) chosen for the exchange-correlation potential $V_{xc}(r)$ of DFT.

We give here a brief summary of the DFT computations of March and Rubio\cite{64}. They were concerned with the way cohesive energies depended on local coordination number $z$ and on bond length. However, unlike the above discussion on the light alkalis, increasing bond length was a focus, due to experiments of Winter \textit{et al.}\cite{65,66} on the heavier alkalis and in particular Rb and Cs. These experiments, both neutron scattering and thermodynamic, were along the liquid-vapour coexistence curve up to the critical point. This was only accessible experimentally for these two alkalis. It was striking from the neutron measurements of the structure factor $S(k)$ that $z$ decreased dramatically from a high value $\sim 8 - 10$ near the triple point to about 2 at the critical point. One of us\cite{67,68} fitted the experimental data for density $d$ by

$$d = az + b$$  

(5.1)

where $a = 0.23$ g cm$^{-3}$ and $b = -0.08$ g cm$^{-3}$ (see also Ref. \cite{69}).

To return now to the calculations of March and Rubio\cite{64}, these LDA calculations by DFT were such that the cohesive energies for mainly K, but also for Rb and Cs, were studied as a function of bond length and coordination number. The essential theoretical predictions are shown in Figs. 1 and 2. The chain structures of Rb and Cs were studied for reasons referred above, though the relevant experiments were
Fig. 2. Same as in Fig. 1 but now for Rb (upper panel) and Cs (lower panel) atoms with long-range order in bcc, diamond, fcc, simple cubic (sc), and linear chain structures ( coordinations $z = 2 - 12$). Redrawn after Ref. [64].

With regard to our emphasis in this review on emergent properties, we note that March and Rubio [64] could interpret their DFT results in terms of dimer potential energy curves, as predicted by March, Tosi, and Klein [71]. The underlying idea of these authors was to decompose the cohesive energy $E(z, r_0)$ into a linear combination of two terms. The first of these is proportional to the coordination number $z$ and is to be viewed as a typical pairwise additive contribution, which can be written in the form $\frac{1}{2} z R(r_0)$, following March et al. [71]. The quantal chemical interpretation of $r_0$ is related to the potassium free-space dimer potential energy curve. The second contribution will be written in the form $-f(z) g(r_0)$, both $R$ and $g$ being related to free-space dimer properties. As March and Rubio [64] emphasize, their DFT results on expanded potassium can be represented very usefully by this simple quantum-chemical approach.

Concerning potassium under pressure, it should be noted that, like Li and Na discussed in Section 5.1, also compressed potassium is characterized by several structural transitions among cubic-like phases, thus confirming the not-so-simple character of the alkalis also in this compound. Numerous works are available in the literature, both experimental and theoretical, and the reader is especially referred to Refs. [72,73,74,75,76,77].
6. Emergent properties in liquid metallic Be

We note here, first of all, the emergence of metallic Be, as we bring Be atoms, initially widely separated, together to eventually form the equilibrium hcp lattice, at zero temperature. The electron density in the unit cell was, as discussed by Matthai et al.\textsuperscript{78}, characterized by marked angularity. Their work\textsuperscript{78} drew heavily on the X-ray Bragg reflection data of Brown\textsuperscript{79} as well as approximate Wannier functions\textsuperscript{14} representing Bloch waves in the NOs. Of course, when Be metal is heated sufficiently, liquid Be, an unpleasant toxic fluid, forms.

Now, when we speak of electron density, it corresponds to taking a ‘snapshot’ of the nuclear positions at a given instant. Since, at the melting temperature, $T_m$ say, of Be metal, the electrons are still essentially totally degenerate fermions, we can proceed to calculate the electron density. But to do practical calculations on the monovalent liquid alkalis, or divalent liquid Be, it is necessary to appeal to ‘neutral pseudoatoms’\textsuperscript{80}\textsuperscript{81}\textsuperscript{82}.

Therefore, Perrot and March\textsuperscript{83}\textsuperscript{84} calculated, by DFT, the electron density $\Delta \rho_{ps}(r)$ associated with such a pseudoatom (ps) for the conduction electrons in liquid metallic Be. Their density $\Delta \rho_{ps}(r)$ is presented in the useful form $Q(r)$ defined such that $Q(r)$ gives the number of (conduction) electrons, two per atom in Be of course, within a sphere of radius $r$ drawn with centre on the nucleus of the chosen pseudoatom. The remarkable oscillations in this $Q(r)$ are then due to the emergent Fermi surface in the metal, taken in the liquid, naturally enough, to be a sphere of radius $k_F$, the Fermi wave number. The oscillations were predicted by Blandin and Friedel\textsuperscript{85} and independently by March and Murray\textsuperscript{86}.

One of the consequences of such a ‘displaced’ charge density around a divalent Be positive ion is a resultant pair potential $\phi(r)$, which, of course, depends on the (now liquid) density of the conduction electrons, Perrot and March\textsuperscript{83}\textsuperscript{84} being concerned only with the liquid metal near $T_m$ at ambient pressure.

If we write $Q(r)$ quite explicitly as

$$ Q(r) = \int_0^r 4\pi r^2 \Delta \rho_{ps}(r) dr, \quad (6.1) $$

then from Poisson’s equation the potential $V_e(r)$ created by the above displaced charge is related directly to $Q(r)$ as follows:

$$ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dV_e}{dr} \right) = -4\pi \Delta \rho_{ps}(r) \quad (6.2) $$

and hence, using Eq. (6.1), one readily obtains

$$ \frac{dV_e}{dr} = - \frac{Q(r)}{e^2}. \quad (6.3) $$

But, as discussed especially by Corless and March\textsuperscript{81},

$$ \phi(r) = -zV(r), \quad (6.4) $$
where $z$ is the valency ($z = 2$, for Be metal). Hence the turning points of the pair potential $\phi(r)$ occur at positions $r$ where

$$\frac{dV}{dr} = \frac{dV_s}{dr} - \frac{z}{r^2} = 0,$$

or

$$Q(r) = z.$$

Fig. 3 shows $Q(r)$ versus $r$, while the Perrot-March pair potential for Be is shown in Fig. 4.

Quite recently, Hoggan and March 87 have compared this pair potential $\phi(r)$ between the (screened) ions in liquid Be with the potential energy curve of the free-space dimer. The free-space dimer has a single (and very shallow) turning point (minimum) not very far from the value $r = 4$ a.u., which can be read off Fig. 4. This stresses, in the context of the present review, the dramatic way the free space dimer potential energy curve is altered in the emergent liquid metal.

While the pair potential in Fig. 4 for liquid Be has not been tested to date, corresponding calculations of Perrot and March 83 for liquid Na can be brought into precise contact with a potential extracted from the measured liquid structure factor $S(k)$. This has been used by Reatto et al. 88,89, following the procedure set out by Johnson and March 90. Therefore, we can plot the Reatto pair potential against the theoretical prediction of Perrot and March 83 for liquid Na nearing the freezing point, and the results are shown in Fig. 5. The lower curve at large $r$ is the experimental prediction of Reatto et al. 88,89, while the other curve is the
Fig. 4. Pair potential $\phi(r)$ for liquid Be. After Ref. [84].

Fig. 5. Pair potentials for liquid Na at $T = 100 \, ^\circ$C and density of 0.929 g cm$^{-3}$. The upper curve for large $r$ is Perrot and March [83] prediction, while lower curve for large $r$ has been derived from inversion of liquid structure factor in the experiments by Reatto et al. [88,89]. After Ref. [83].

All the main features are seen to be accurately predicted by the electron theory.
7. Phenomenological theory of first- and second-order metal-to-insulator (MI) transitions at $T = 0$

Below, a phenomenological theory of metal-to-insulator (MI) transitions at $T = 0$ will be outlined, in which the discontinuity $q$ in the single-particle occupation probability $n(p)$ at the Fermi surface is the order parameter. We apply it to the case of the second order MI transition in a half-filled Hubbard band. The enhancement of the spin susceptibility by the Hubbard interaction will also be discussed. Going back to jellium already discussed above, the same phenomenology is applied here, but now a first order MI transition occurs when the conduction electron liquid crystallizes onto the Wigner lattice.

7.1. Spin susceptibility near metal-to-insulator (MI) transition

Then, following March et al.,

$$E(m, q) = R_0 + a m^2 - h m + E_1 q + E_2 q^2 + \ldots + eqm^2.$$  \hspace{1cm} (7.1)

Minimizing with respect to $m$ yields

$$2a m + 2eqm = h,$$  \hspace{1cm} (7.2)

and hence the spin susceptibility $\chi$ can be read off from

$$m = \frac{1}{2} [a(U) + eq]^{-1} h \equiv \chi h,$$  \hspace{1cm} (7.3)

where $U$ denotes the on-site repulsion within Hubbard model. If a transition of the second order occurs at a critical value $U = U_c$, then $q \to 0$ as $U \to U_c$, and the physical question as to the enhancement of $\chi$ as the MI transition is approached rests on the behaviour of $a(U)$ as a function of the Hubbard interaction $U$. Provided $a \to 0$ as $1 - U/U_c$ or faster, it can be shown that

$$\chi \propto \left(1 - \frac{U}{U_c}\right)^{-1}.$$  \hspace{1cm} (7.4)

This has been discussed also by Brinkman and Rice in relation to experiments on $V_2O_3$ which indeed show enhancement of $\chi$ by $U$ in the metallic phase as the MI is approached.

7.2. Magnetic susceptibility of expanded fluid alkali metals

Related to the above phenomenology of a correlation-induced MI transition, Chapman and March have proposed an interpretation of the behaviour of the magnetic susceptibility of expanded fluid metals. Renormalization of the Fermi temperature caused by correlation is shown to play a major role. An important conclusion of Chapman and March is that the momentum distribution at the Fermi surface is quantitatively very different from jellium at the same density.
8. Jellium in two-dimensions in an applied magnetic field

8.1. Magnetically induced quantal Wigner solid as produced in GaAs/AlGaAs heterojunction

Magnetically aided quantal Wigner electron crystals were first predicted theoretically in 1968 by Durkan et al. (DEM)\textsuperscript{[94].} These authors were motivated by experiments of Putley\textsuperscript{[95]} on highly compensated \( n \)-type InSb. Putley observed conduction in an impurity band as a function of applied magnetic field of strength \( B \), which however was found experimentally to be suppressed at a critical magnetic field \( B_c \) as \( B \) was gradually increased. DEM argued that, at this transition, Wigner quantal electron crystallization was occurring. Subsequent experiments by Somerford\textsuperscript{[96]} on the same system were interpreted by Care and March\textsuperscript{[97]} as a Wigner transition aided by the magnetic field. Later, Kleppmann and Elliott\textsuperscript{[98]} pressed this interpretation and showed that the anisotropy of the conductivity measured by Somerford was consistent with the Wigner transition.

Some 20 years after the above proposal of DEM, interest in the magnetically induced Wigner electron solid (MIWS) was revived by the beautiful experiment of Andrei et al.\textsuperscript{[99]} on a two-dimensional electron assembly in a GaAs/GaAlAs heterojunction. These authors pointed out that an essential difference between an electron liquid (delocalized state) and a quantal Wigner electron solid is that it is only the latter phase that can sustain low frequency shear waves. Evidence was presented by Andrei et al.\textsuperscript{[99]} that their 2D electrons, in a sufficiently strong magnetic field perpendicular to the plane of the electron assembly, could support shear waves.

Lea et al.\textsuperscript{[100]} gave the thermodynamics of the melting of a 2D electron assembly in a magnetic field. Their theoretical study was prompted by the experiment of Buhmann et al.\textsuperscript{[101]} on the luminescence spectrum of a heterojunction. This led these authors to sketch the melting curve of the Wigner solid as a function of the Landau level filling factor \( \nu \). This is defined in terms of the (areal) electron density \( n \) and the magnetic field strength \( B \) by

\[
\nu = nhc/eB.
\] (8.1)

The schematic diagram sketched by Buhmann et al.\textsuperscript{[101]} has been interpreted thermodynamically by Lea et al.\textsuperscript{[100]} and the main results are summarized in Figs. 6 and 7.

Lea et al.\textsuperscript{[100]} noted first that the thermodynamics of an electron crystal to electron liquid first-order melting transition leads for the melting temperature \( T_m \) as a function of magnetic field to the result, at constant area \( \Omega \),

\[
\left( \frac{\partial T_m}{\partial B} \right)_\Omega = -\frac{\Delta M}{\Delta S}.
\] (8.2)

Denoting the crystal phase by subscript \( C \) and the liquid by \( L \), then \( \Delta M = M_L - M_C \) is the change of magnetization on melting, while \( \Delta S = S_L - S_C \) is the corresponding change in entropy. This is then cast by Lea et al.\textsuperscript{[100]} in terms of the Landau filling
Fig. 6. Schematic phase diagram as proposed by Buhmann et al.\cite{101}, showing the four crystal phases, \(C_1\) to \(C_4\), and the reentrant liquid phase at \(\nu = \frac{1}{9}, \frac{1}{7}, \) and \(\frac{1}{5}\). Ordinate show the melting temperature \(T_m\), normalized with respect to that of a classical one-component plasma\cite{99} \(T_{mc} = \pi^2(\pi n)^{1/2}/n k_B \Gamma_m\), where \(k_B\) is Boltzmann’s constant, \(\kappa\) the dielectric constant of the host material, and \(\Gamma_m = 127 \pm 3\) (see Ref.\cite{100} and references therein). Symbols mark the points \(\Delta M, \Delta S, \Delta E = 0\), as deduced from thermodynamics. Redrawn after Ref.\cite{100}.

\[
\Delta S = 0 \quad \circ \quad \Delta E = 0 \quad \bullet \quad \Delta M = 0 \quad \triangle
\]

\[
\frac{T_m}{T_{mc}}
\]

\[
\nu \quad 0 \quad 0.05 \quad 0.1 \quad 0.15 \quad 0.2 \quad 0.25 \quad 0.3 \quad 0.35 \quad 0.4
\]

\[
C_1 \quad C_2 \quad C_3 \quad C_4
\]

Fig. 7. Schematic diagram of the change in magnetization \(\Delta M\) on melting along the melting curve shown in Fig. 6. Redrawn after Ref.\cite{100}.

\[
\frac{\partial T_m}{\partial \nu} \bigg|_{\Omega} = \frac{B}{\nu} \frac{\Delta M}{\Delta S}.
\] (8.3)
The phase diagram in Fig. 6 showing the equilibrium melting curve between the Wigner electron solid and the Laughlin electron liquid shows four crystal phases $C_1$ to $C_4$, and the relevant liquid phase at $\nu = \frac{1}{9}, \frac{1}{7},$ and $\frac{1}{5}$. The reader interested in finer details should consult the work of Lea et al. 100.

8.2. Anyon magnetism in the Laughlin liquid near the melting curve of the Wigner electron solid

After their thermodynamic understanding of the above melting curve, Lea et al. 100 sought macroscopic understanding of especially the change in magnetization $\Delta M$ across the melting curve. It then became clear that most of the remarkable features of the melting curve must reside in the magnetism of the Laughlin liquid near the melting temperature. And since knowledge of the magnetism of the Wigner electron solid pointed to weak antiferromagnetism, $\Delta M$ must come from the 2D electron liquid. This led to the treatment of anyon magnetism, due to the fact that in 2D the electron liquid obeyed anyon 102,103,104 rather than Fermi statistics.

To complement the above thermodynamics, the magnetism of the Laughlin liquid was studied by Lea et al. 100 using the anyon model (see also Refs. 105,106 and references therein on fractional statistics). Assuming this dominates $\Delta M$ in the thermodynamics, since the Wigner solid exhibits only weak cooperative magnetism, Lea et al. 100 drew a schematic diagram (Fig. 7) of the change in magnetization on melting along the melting curve shown in Fig. 6. As these authors stressed, the field dependence of $\Delta M$ is very reminiscent of the de Haas-van Alphen effect 14 at integral values of $\nu$.

To conclude this brief discussion, we should note that Wu et al. 107 (see also Ref. 108) have given a detailed theoretical treatment of the thermal activation of quasiparticles and the thermodynamic observables in fractional quantum Hall (FQH) liquids. But their final sentence is relevant to the work of Lea et al. 100 under discussion here. This sentence reads: ‘In particular, it is more desirable that these theoretical predictions 107 would be put to experimental tests, if the tremendous difficulties in measuring thermodynamic quantities of a thin layer of electron gas could be overcome someday.’ It is therefore the more remarkable that existing experiments on GaAS/AlGaAs heterojunctions in magnetic fields $B$ perpendicular to the two-dimensional electron assembly can provide crucial insight into some of the thermodynamic quantities characterizing the FQH liquid studied theoretically by Wu et al. 107.

9. Summary and future directions

Though different in emphasis from the approach adopted in the present review, it is relevant here to refer to a body of work on bonding and information theory. The interested reader is recommended to start by using especially the early references in the article by Nalewajski 109. In this particular article, the focus is on $H_2$, a comparison being made between the valence bond treatment and communication
theories. In the above context, further insight has been obtained into the work of Hirshfeld. Relevant references can also be found in Parr et al. In relation to emergent properties, the correction between quantum entanglement and correlation in many-body assemblies is considered in the work of Campos Venuti et al.

To conclude, we want to refer again to the relevance of quantum information theory in many-body theory. In particular, we recommend the reader to consult the discussion of Schollwöck (see especially section C). Schollwöck stresses in particular, in quantum chemistry applications, the importance of the entanglement entropy. The work of Legeza and Sólyom is another good starting point for the interested reader. Finally, for the reader needing further details on quantum information, we recommend study of the book by Nielsen and Chuang.

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Appendix A. Relation between three forms of quantum information entropy for a whole class of two-electron spin-compensated models

Holas et al. have solved for the 1DM a class of models for two-electron spin-compensated atomic ions. Below, we first summarize the essence of their results and then use these to set out a route for relating the three forms of quantum information entropy set out in Eqs. (3.1), associated with the name of Shannon, plus Eq. (3.2), defining Jaynes entropy.

For the case when we choose the constants in Eqs. (3.1) as $-1$, to accord for example with Hornyárik and Nagy (see also Ref. 119), who give an Uncertainty Principle inequality satisfied by the Shannon forms sum $S_\rho + S_n$, namely

$$S_\rho + S_n \leq 1 + \ln \pi. \tag{A.1}$$

It is proposed below how one can, in the future, numerically test the utility of this inequality for the above class of two-electron artificial atoms. Also, the relation between the 1DM and the electron density $\rho(r)$ will be given for the Moshinsky model in which both external potential $V_{\text{ext}}$ and interaction $u(r_{12})$ have harmonic forms.

The essence of Holas et al. was to separate the center of mass (cm) part
from the relative motion \((rm)\) part of the ground-state wave function as

\[
\Psi(r_1, r_2) = \Psi_{cm}\left(\frac{r_1 + r_2}{2}\right) \Psi_{rm}(|r_1 - r_2|). \tag{A.2}
\]

The latter \(rm\) part solves the one-body Schrödinger equation with effective potential \(V_{\text{eff}}(r) = V_{\text{ext}}(r) + \text{const} \times u(r_{12})\). The analytical form of the cm part is \[117\]

\[
\Psi_{cm}(R) = \exp\left(-\frac{1}{2\alpha_{cm}^2} \right), \quad \tag{A.3}
\]

where \(\alpha_{cm} = (k/2m\omega_0)^{1/2}\), and \(\omega_0^2 = k/m\). Writing the \(rm\) wave-function as \(\Psi_{rm}(r) = \text{const} \cdot \psi_{rm}(r)/r\), the one-body Schrödinger equation below results:

\[
\left[-\frac{\hbar^2}{2m_{rm}} \left(\frac{d}{dr}\right)^2 + \frac{1}{2} m_{rm}\omega_0^2 r^2 + u(r)\right] \psi_{rm}(r) = E_{rm}(r) \psi_{rm}(r). \tag{A.4}
\]

Holas et al. \[117\] obtained \(\gamma(r, r')\) exactly by quadrature on \(\Psi_{cm}\) and \(\psi_{rm}\). However, the form of \(\gamma\) is somewhat complex, so below we limit ourselves to reporting \(\gamma(r, r')|_{r=r'} = \rho(r)\) explicitly for general \(u(r)\) as

\[
\rho(r) = \frac{8}{\sqrt{\pi}} e^{-r^2/\alpha_{cm}^2} \int_0^\infty dy y^2 e^{-y^2/4} |\Psi_{rm}(\alpha_{cm}y)|^2 \sinh(\alpha y/\alpha_{cm}) \sinh(\alpha_{cm}y). \tag{A.5}
\]

One can solve Eq. (A.5) by Fourier transform (FT) to obtain \(\Psi_{rm}\) in terms of the FT of \(\rho(r)\); usually called the atomic scattering factor \(f(k)\). But \(\gamma(r', r)\), the exact 1DM, is also known as characterized by \(\Psi_{cm}\). Therefore, for this class of models, the three information entropies can all be related to the diagonal density \(\rho(r)\), most elegantly in terms of the scattering factor \(f(k)\).

For the Moshinsky atom, Holas et al. \[117\] obtained the relation between the 1DM \(\gamma\) and the ground-state density \(\rho(r)\) as

\[
\gamma(r_1, r'_1) = \left(\frac{\rho(\bar{r})}{\rho(r_0)}\right)^{\alpha^2/(2\alpha - 1)}, \tag{A.6}
\]

where \(r_0 = \frac{1}{2}(r_1 + r'_1)\), \(\bar{r} = [\frac{1}{2}(r_1^2 + r'_1^2)]^{1/2}\), and the ‘interaction strength’ parameter \(\alpha\) is defined as

\[
\alpha = \frac{1}{2} \left(1 + \sqrt{1 + 2K}\right), \tag{A.7}
\]

which can in fact be related to the density \(\rho(r = 0)\) by

\[
\alpha^{-1} = 2 - \pi[\rho(r = 0)/2]^{2/3}. \tag{A.8}
\]

Eq. (A.6) above agrees with the earlier result given by March \[121\] apart from the normalization factor. Holas et al. \[117\] also showed that the kinetic energy density for the Moshinsky atom is related to the ground-state density \(\rho(r)\) as

\[
t(r) = \frac{1}{2} \rho(r) \left(\frac{3(\alpha - 1)^2}{2 - \alpha} - \frac{2\alpha - 1}{\alpha} \ln \frac{\rho(r)}{\rho(0)}\right). \tag{A.9}
\]

Fig. A.1 shows a plot of the correlation kinetic energy against Jaynes entropy for the Moshinsky atom\[1\].
Fig. A1. Correlation kinetic energy against Jaynes entropy, both in atomic units, for the Moshinsky atom. Redrawn after Ref. [1].

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