A model for divalent-atom systems—one dimension†

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Abstract. A one-dimensional system, with L sites and periodic boundary conditions, is considered. N divalent atoms occupy sites. The atoms have two orbitals, electron hopping is allowed between nearest neighbour atoms, and intra-atomic electron correlation is taken into account. The ground and first excited many-body states are estimated using a basis, appropriate to weak interatomic coupling, in which multiple nearest neighbour resonating valence bond excitations, appropriately symmetrised, are included. Ordered and disordered systems are considered, for large L.

1. Introduction

There are a great deal of experimental data on the electronic and thermodynamic properties of mercury for densities ranging from that of the solid, through the expanded liquid regime, to gaseous densities [1]. The liquid, at coexistence with its vapour, is known to be metallic down to densities of approximately 1.6 times the critical density for the vapour–liquid phase transition ($\rho_c = 5.77 \text{ g cm}^{-3} = 1.7 \times 10^{22}$ atoms cm^{-3}). Neutron scattering data for expanded metals indicate that, on expansion, the number of nearest neighbours (NN) decreases while the NN distance is almost constant [2]. Such data have led to a model of expanded liquid mercury in which a background lattice (fixed NN distance) is occupied by atoms and vacancies, with the fraction of atoms adjusted to fit the experimental density. Based on this model, there has been the suggestion that metallisation ocurs when atoms have 'sufficient' numbers of NN, and such a 'sufficiency' percolates through the system. A random vacancy distribution was postulated in that model [3]. We have decided to pursue the properties of divalent-atom systems with the motivation noted above.

2. Our model

We propose to study a particularly simple model in which the level of approximation is well defined. As a preliminary exercise we have studied the one-dimensional system of L sites (periodic boundary conditions) occupied by N atoms ($N \leq L$). Each atom has

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† A preliminary reeport on part of this work was presented at the 7th International Conference on Liquid and Amorphous Metals (LAM 7), Kyoto, Japan, to be published as a special issue of the *Journal of Non-Crystalline Solids* and edited by Professor H Endo.

two orbitals (labelled s and p) and the atomic Hamiltonian describing low energy states includes correlations:

$$H_a = \sum_\sigma [\varepsilon_s n_{s\sigma} + \varepsilon_p n_{p\sigma} + (U_s/2)n_{s\sigma}n_{s\sigma'} + U_{sp\uparrow\downarrow}n_{s\sigma}n_{p\sigma'} + U_{sp\uparrow\uparrow}n_{s\sigma}n_{p\sigma}]$$

with σ a spin label and σ' the opposite spin, s labelling the lower atomic orbital and p the upper, the ε representing one-electron energies, U representing correlation energies, and the n being appropriate fermion number operators.

The atomic Hamiltonian is diagonal in the same basis as are S^2 and S_z. The low energy states of the neutral, divalent atom (A^0) can be represented by the spin singlets with energies

$$2\varepsilon_s + U_s \equiv 0 \qquad \varepsilon_s + \varepsilon_p + U_{sp\uparrow\downarrow} \equiv B$$

and the spin triplets ($S_z = 0, \pm1$) with energies

$$\varepsilon_s + \varepsilon_p + U_{sp\uparrow\downarrow} \equiv B \qquad \varepsilon_s + \varepsilon_p + U_{sp\uparrow\uparrow} \equiv B'.$$

The five atomic parameters can be related to the excitation energies B and B' of the neutral atom, the excitation energy of A^+, and the ionisation potentials of A^+ and A^0. Thus the typical values for an atom resembling Hg would be of order (in eV):

$$\varepsilon_s = -8.4 \qquad \varepsilon_p = 1.5 \qquad B = 6.7 \qquad B' = 4.9.$$

The low energy states of a collection of such atoms placed on a lattice, with sites labelled by i and NN sets labelled $\langle i, j\rangle$, can be described by

$$H = \sum_i H_{ai} + \sum_{\langle i,j\rangle} [t_{sp}(c_{is\sigma}^+ c_{jp\sigma} + c_{ip\sigma}^+ c_{js\sigma}) + t_{ss}c_{is\sigma}^+ c_{js\sigma} + t_{pp}c_{ip\sigma}^+ c_{jp\sigma}]$$

with c^+ and c being fermion creation and annihilation operators and the t representing NN hopping matrix elements. For typical atoms under consideration, the ratios $t/U \ll 1$. Again for Hg-like atoms, reasonable numerical values (in eV) are $t_{sp} = 0.44$, $t_{ss} = -0.41$, $t_{pp} = 0.69$ (giving the cohesion of the free dimer as approximately 60 meV) [4]. The auxiliary definition of the energy of a charge transfer pair of atoms, $C = B + U_{sp\uparrow\uparrow}$ ($\simeq 13$ eV) is useful. Note that the interatomic couplings do not flip spins.

For small t/U, examination of the free dimer (no periodic BC) and the ring trimer set the stage for obtaining results for the L-site ring with L atoms, and with N ($<L$) atoms, in the limit $L \to \infty$ and, then, also $N \to \infty$ with $N/L = \rho$. For the dimer, the states can be classified as eigenstates of S^2, S_z, and site interchange ($+$: totally symmetric; $-$: antisymmetric). A restricted basis suffices, for small t/U, to make the Hamiltonian block-diagonal

$$00+: \begin{vmatrix} 0 & 2t_{sp} & 0 \\ 2t_{sp} & C & t_{pp} - t_{ss} \\ 0 & t_{pp} - t_{ss} & B \end{vmatrix} \qquad 00-: \begin{vmatrix} C & -(t_{ss} + t_{pp}) \\ -(t_{ss} + t_{pp}) & B \end{vmatrix}$$

$$10+: \begin{vmatrix} C & t_{ss} - t_{pp} \\ t_{ss} - t_{pp} & B \end{vmatrix} \qquad 10-: \begin{vmatrix} C & t_{ss} + t_{pp} \\ t_{ss} + t_{pp} & B \end{vmatrix}$$

$$1 \pm 1+: \begin{vmatrix} C & t_{ss} - t_{pp} \\ t_{ss} - t_{pp} & B' \end{vmatrix} \qquad 1 \pm 1-: \begin{vmatrix} C & t_{ss} + t_{pp} \\ t_{ss} + t_{pp} & B' \end{vmatrix}.$$

The basis states for $00+$ are

$$(R_1 s\uparrow \ R_1 s\downarrow \ R_2 s\uparrow \ R_2 s\downarrow)$$

$$\tfrac{1}{2}\{[(R_1s\uparrow \; R_1s\downarrow \; R_1p\uparrow \; R_2s\downarrow) - (R_1s\uparrow \; R_1s\downarrow \; R_1p\downarrow \; R_2s\uparrow)]$$

$$+ [(R_2s\uparrow \; R_2s\downarrow \; R_2p\uparrow \; R_1s\downarrow) - (R_2s\uparrow \; R_2s\downarrow \; R_2p\downarrow \; R_1s\uparrow)]\}$$

$$\tfrac{1}{2}\{[(R_1s\uparrow \; R_1p\downarrow \; R_2s\uparrow \; R_2s\downarrow) - (R_1s\downarrow \; R_1p\uparrow \; R_2s\uparrow \; R_2s\downarrow)]$$

$$+ [(R_2s\uparrow \; R_2p\downarrow \; R_1s\uparrow \; R_1s\downarrow) - (R_2s\downarrow \; R_2p\uparrow \; R_1s\uparrow \; R_1s\downarrow)]\}$$

with the parentheses implying normalised anti-symmetrisation with respect to electron interchange, where R_i labels the site, s or p the atomic orbital, and the arrows the z component of the electron spin. Thus, the square brackets enclose spin singlets (NN resonating valence bond (RVB) states) and it can be seen the states are symmetric with respect to site interchange. The bases for the remaining Hamiltonian blocks are clear generalisations of the above. Already, the inclusion of the state with diagonal element B in 00+ only contributes corrections of order $(t/U)^4$ to the ground state, while similar contributions from other states in the basis (the one at $2B$, for example) have been ignored, as have those yielding even higher order energy corrections, in t/U. This state is included to give an explicit example of such effects and similar states must be included to lowest order in the trimer and larger rings. For the remaining symmetries, the lowest state of each is obtained from the blocks above, to order $(t/U)^2$.

To the lowest order, the dimer states consist of an isolated 00+ ground state at

$$-\alpha^2 C\{1 + [(t_{pp} - t_{ss})^2/BC - \alpha^2]\}$$

with $\alpha = 2t_{sp}/C$, the square bracket showing the difference of fourth-order contributions. The lowest energy excitation gap (00+ to $1 \pm 1+$ or 10+, depending on whether B' or B is smallest, and assuming t_{ss} and t_{pp} have opposite sign) has

$$\Delta_{2(11+)} = B' + \left[1 - \frac{C}{4(C - B')}\left(\frac{t_{ss} - t_{pp}}{t_{sp}}\right)^2\right]\alpha^2 C$$

(for $\Delta_{2(10+)}$: replace B' by B in above), to order $(t/U)^2$.

The ring trimer has a special feature in that all three sites are mutually nearest neighbours. To lowest order, the ground state is again 00+ (now totally symmetrised over the three sites). Its energy is $-3\alpha^2 C$, which is obtained by admixing to the atomic ground state (at 0) a fully symmetrised, charge transfer RVB. Assuming $B' < B$, the lowest excited state is 11+ and arises from diagonalising

$$\begin{vmatrix} B' & \sqrt{2}(t_{ss} - t_{pp}) & 2t_{sp} \\ \sqrt{2}(t_{ss} - t_{pp}) & C - (t_{ss} - t_{pp}) & \sqrt{2}t_{sp} \\ 2t_{sp} & \sqrt{2}t_{sp} & B' + C \end{vmatrix}$$

yielding, to lowest order, an energy of

$$B' - \left[1 + \frac{C}{2(C - B')}\left(\frac{t_{ss} - t_{pp}}{t_{sp}}\right)^2\right]\alpha^2 C.$$

(Again, let B replace B', if it is smaller, to get the lowest 10+ state.) Hence,

$$\Delta_{3(11+)} = B' + \left[1 - \frac{C}{4(C - B')}\left(\frac{t_{ss} - t_{pp}}{t_{sp}}\right)^2\right]2\alpha^2 C.$$

3. Long ordered rings

An estimate for the ground state of the L-atom ring (large L) is easily obtained (to order $(t/U)^2$) by diagonalising a tridiagonal block of $00+$ symmetry states: coupling the atomic ground state to a symmetrised state with one charge transfer RVB excitation, and it to one with two symmetrised RVBs (all charge transfer is to NN), etc. The equal spacing of the diagonal matrix elements and the tridiagonal form allow rewriting H in terms of boson creation and annihilation operators (a^+ and a) as

$$H = a^+aC + \alpha C(fa^+ + af) \qquad f = [(L + 2 - 2a^+a)(L + 1 - 2a^+a)/(L - a^+a)]^{1/2}.$$

For large L and small α, an expansion of f is appropriate. Keeping two corrections for large L yields

$$H/C = [a^+a + \alpha\sqrt{L}(1 + 3/2L - 1/8L^2)(a^+ + a)]$$
$$- (\alpha/8\sqrt{L})(12 + 17/L)(a^+a^+a + a^+aa).$$

The definition: $b = a + \alpha\sqrt{L}(1 + 3/2L - 1/8L^2)$, with $[b, b^+] = 1$, diagonalises the square bracket and yields

$$H/C = -[\alpha^2 L(1 - 3\alpha^2) + 3\alpha^2(1 - \tfrac{71}{12}\alpha^2) + (2\alpha^2/L)(1 - \tfrac{153}{8}\alpha^2)]$$
$$+ b^+b[1 + 6\alpha^2(1 + 35/12L)] - (3\alpha^3\sqrt{L}/8)(12 + 17/L)(1 + 3/2L$$
$$- 1/8L^2)^2(b^+ + b) + (\alpha^2/8)(1 + 3/2L - 1/8L^2)(b^+b^+ + bb)$$
$$- (\alpha/8\sqrt{L})(12 + 17/L)(b^+b^+b + b^+bb) + \text{higher order terms}.$$

It can be seen that further transformations, adding a constant to b, yield higher order corrections ($O(\alpha^6)$) to the ground state and $O(\alpha^4)$ to the separation between these states. For small enough α^2 the expansion is convergent but, in limiting the basis, we neglected corrections of order α^4, hence the above is exact to order α^2 and large L:

$$H/C = -\alpha^2[L + 3 + 2/L] + b^+b[1 + 6\alpha^2(1 + 35/12L)].$$

The constant term gives the ground state binding of the L-atom ring. (The $00+$ excitations are not especially interesting since we know they do not give rise to the lowest energy excitation; in fact such a state is not even the lowest at an energy $\simeq C$ above the ground state.) The ground state eigenvector can also be obtained using the original $00+$ basis of q symmetrised charge transfer RVBs, for small t/U:

$$|gd\rangle = \sum_{q=0}^{L/2} d_q|q\rangle \qquad \text{with } b|gd\rangle = 0 \text{ and } a|q\rangle = \sqrt{q}|q - 1\rangle.$$

Thus,

$$g(q) \equiv |d_q/d_0|^2 = (\alpha^2 L)^q/q!$$

which, for large L, peaks at

$$q_0 = \alpha^2 L - \tfrac{1}{2} - (1/4\alpha^2 L)^2 + \ldots.$$

For q near q_0:

$$g(q) = [(1/2\pi\alpha^2 L)^{1/2} \exp(\alpha^2 L)] \exp - [(q - q_0)^2/2(\tfrac{2}{5}\alpha^2 L)].$$

The ground state has an average of $\alpha^2 L$ symmetrised ($00+$) charge transfer RVBs, with a variance of $[\tfrac{2}{5}\alpha^2 L]^{1/2}$, on the L sites.

From the dimer and trimer results, it is deduced that the first excitation of the L-site ring should be at an excitation energy near B' (11+) or B (10+), whichever is smaller (we assume B' in what follows but if it were B, the result would be obtained by replacing B' by B). The 11+ basis states are constructed by appropriate symmetrisation of a B' excitation ($|0s\rangle$) which couples to one with a B' excitation and a singlet charge transfer RVB ($|1s\rangle$), as well as to another, with a triplet charge transfer excitation (at NN) ($|0t\rangle$). Other states in the basis are $|ps\rangle$: a B' excitation and p singlet, charge transfer RVBs; and $|pt\rangle$: a triplet NN charge transfer excitation and p singlet, charge transfer RVBs ($p = 1$, $2 \ldots$). The 11+ block of H has non-zero elements

$$H_{0s,0s} = B' \qquad H_{ps,ps} = B' + pC \qquad H_{pt,pt} = (p + 1)C$$

$$H_{(p-1)s,ps} = [p(L - 2p + 1)(L - 2p)/(L - p)]^{1/2}\alpha C$$

$$H_{ps,pt} = [2(L - 2p + 1)/(L - p - 1)]^{1/2}(t_{ss} - t_{pp})$$

$$H_{0t,1t} = (L - 3)^{1/2}\alpha C$$

$$H_{(p-1)t,pt} = [p(L - 2p)(L - 2p - 1)/(L - p - 1)]^{1/2}\alpha C \qquad \text{for } p > 1$$

with appropriate adjoints. Note that, in contrast to the ring trimer, $H_{0t,1s} = 0$ since no site is neighbour to a pair of nearest neighbours.

By first diagonalising the coupling between $|ps\rangle$ and $|pt\rangle$, one obtains $O(\alpha^2)$ corrections to the diagonal elements, and $O(\alpha^2)$ couplings between these corrected states (they may be ignored, as they give $O(\alpha^4)$ corrections to the energy—comparable to those ignored in limiting the basis). The block is thus brought into two, decoupled, tridiagonal blocks with bases

$$|ps_c\rangle = |ps\rangle + [2(L - 2p - 1)/(L - p - 1)]^{1/2}[(t_{pp} - t_{ss})/(C - B')]|pt\rangle$$

$$|pt_c\rangle = |pt\rangle - [2(L - 2p - 1)/(L - p - 1)]^{1/2}[(t_{pp} - t_{ss})/(C - B')]|ps\rangle$$

normalised to order t/U. The lowest state of this symmetry comes from the $|ps_c\rangle$ block. It may be rewritten, with boson creation and annihilation operators, as

$$H = B' + a^+aC - [2(t_{pp} - t_{ss})^2/(C - B')][(L - 1 - 2a^+a)/(L - 1 - a^+a)]$$
$$+ \alpha C(f_1 a + a^+f_1)$$

with

$$f_1 = \{[(L + 1 - 2a^+a)(L - 2a^+a)]/(L - a^+a)\}^{1/2}.$$

Using the same technique as previously, to order α^2 and L^{-1}, the lowest excited state is to be found at

$$B' - \alpha^2 CL\left\{1 - \frac{1}{L}\left[1 - \frac{C}{2(C - B')}\left(\frac{t_{pp} - t_{ss}}{t_{sp}}\right)^2\right] - \frac{7}{8L^2}\right\}.$$

Thus the lowest excitation gap is

$$\Delta_{L(11+)} = B' + 4\alpha^2 C\{1 - [C/8(C - B')][(t_{pp} - t_{ss})/t_{sp}]^2 + 23/32L\}$$

which may be smaller or larger than B', depending on the curly brackets; but the value is near B' since α^2 is small. This lowest energy excitation has a B' excitation and an average of $\alpha^2 L$ singlet, charge transfer, RVBs appropriately symmetrised, with a small admixture of a triplet charge transfer excitation at NN, and $\alpha^2 L$ singlet, charge transfer RVBs, also appropriately symmetrised (to lowest order in α).

For small α, the L-atom ring remains insulating as $L \to \infty$: to lowest order, only NN charge separation is obtained and the gap is finite. In higher dimensions, the new coupling constant will be $\alpha^2 = 2z(t_{sp}/C)^2$, where z is the coordination number (the factor of 2 is spin); special cases arise in structures with sites that are nearest neighbours to nearest neighbours (the ring trimer, honeycomb, and FCC structures, for example). It seems clear that metallisation in these ordered systems requires going beyond weak coupling (higher order terms in α^2) to allow charge separation beyond NN.

4. Disordered rings

In the spirit of the above discussion, we consider a simple extension to a disordered system. The introduction of vacancies into the ring (disorder) merely introduces finite line segments in which electronic hopping can take place. To lowest order in α, the ground state of such a segment, with r atoms, has $00+$ symmetry and lies at $-\alpha^2 C(r - 1)$. If atoms are allowed to hop into NN vacancies in order to minimise the free energy of the system (with a total number of sites L and a total number of atoms N, with $L, N \to \infty$ and $N/L = \rho$), the calculation at thermal equilibrium is straightforward, without further assumptions on the atomic and vacancy distributions.

The probability that all the vacancies are together, in which case the system has only one segment, is

$$P_1 = \left[\sum_{n=1}^{\min[L\rho, L(1-\rho)]} e^{-a(n-1)} \frac{1}{n} \binom{L\rho - 1}{L\rho - n} \binom{L(1-\rho) - 1}{L(1-\rho) - n} \right]^{-1}$$

where $a \equiv \alpha^2 C/k_B T$ and parentheses enclose binomial coefficients. The probability that the system has n line segments of atoms (P_n) is the nth term in the above sum, multiplied by P_1. If we further specify that there are a total of n segments but that n_1 segments have L_1 atoms, n_2 have L_2 atoms, etc, with

$$\sum_i n_i = n \qquad \sum_i n_i L_i = L\rho$$

then

$$P_{\{n_i\}} = P_n \bigg/ \prod_i n_i!.$$

However, the internal energy of the system only depends on the total number of segments:

$$E_n - E_1 = \alpha^2 C(n - 1).$$

Note that it has been assumed that $k_B T \ll B', B$. This is reasonable, since $\alpha^2 C/k_B \simeq 10^3$ K and $B'/k_B \simeq 6 \times 10^4$ K, for typical systems and temperatures of interest.

The peak of the distribution is at a number of segments n_0:

$$n_0/L \equiv x = [1/2(e^a - 1)]\{-1 + [4\rho(1 - \rho)(e^a - 1) + 1]^{1/2}\}.$$

The distribution is Gaussian with a standard deviation

$$\sigma_n^2/L = [x(\rho - x)(1 - \rho - x)]/[2\rho(1 - \rho) - x].$$

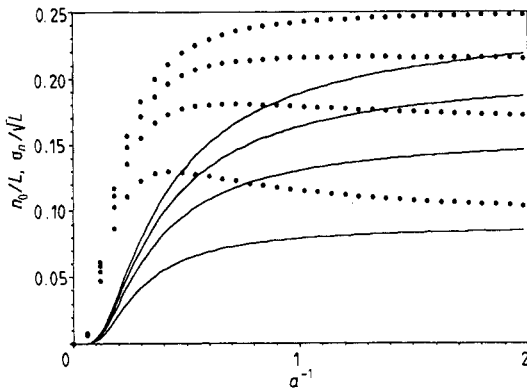These functions are plotted, for various ρ, as a function of a^{-1} in figure 1.

Figure 1. Number of segments, peak and variance, of the disordered ring with a large number of sites (L), at fractional occupation ρ, versus $a^{-1} = k_B T / \alpha^2 C$. Full curves are the peak values; dotted curves are the variances, for various values of ρ (top to bottom: $\rho = 0.5$; 0.3 and 0.7; 0.2 and 0.8; 0.1 and 0.9).
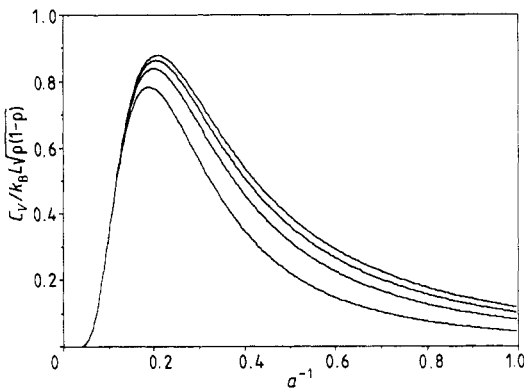

Figure 2. Specific heat results, given as $C_V / k_B L [\rho(\rho - 1)]^{1/2}$ versus a^{-1}. Top to bottom: $\rho = 0.5$; 0.3 and 0.7; 0.2 and 0.8; 0.1 and 0.9.

The average energy of the system is

$$\bar{E} = \sum_n (-\alpha^2 CL)(\rho - n/L)P_n = -\alpha^2 CL(\rho - x).$$

So, for example, the specific heat at constant L and ρ is

$$C_V = \alpha^2 CL(\partial x / \partial T)|_{L,\rho}.$$

It is plotted, for various ρ, as a function of a^{-1} in figure 2. It should be noted that the temperature at which it peaks is $a^{-1} \simeq 0.2$ with a weak density dependence in the interval $0.1 \leqslant \rho \leqslant 0.9$.

5. Summary

Motivated by experimental data on the properties of fluid mercury, we have begun to study a well defined, simple model for disordered, divalent-atom systems. The preliminary work reported here concerns divalent two-level atoms in a one-dimensional structure, for weak interatomic coupling. The ordered system is insulating in the thermodynamic limit. The disordered system has all states localised. Our preliminary conclusion regarding higher-dimensional ordered systems is that the important parameter will be

$2z(t_{sp}/C)^2$ and that the system may be metallic if this parameter is not very small. Qualitatively this conclusion supports the speculation that the experimental system becomes metallic if there are 'sufficient' nearest neighbours and this 'sufficiency' percolates through the disordered atom-vacancy alloy [3]. Calculations in two and three dimensions have been undertaken and will be reported in the future.

Acknowledgments

References

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