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Pseudopotentials and the Theory of High T $_{\text{c}}$ Superconductivity [and Discussion]

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Pseudopotentials and the theory of high T_c superconductivity

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I present two very different uses of the idea of pseudopotentials in the theory of cuprate superconductors. In the first, the 'chemical pseudopotential' scheme is used to set up the underlying Hubbard model which is appropriate for these substances; in the second, I show that the conventional multiple-scattering technique for constructing an effective scattering length theory does not converge for the two-dimensional Hubbard model.

When working on the subject which has been engrossing me for the past four years, high T_c superconductivity, I often feel that I should be disqualified from the competition because of the fact that I carry a number of concealed weapons on me, not the least of which is the understanding of pseudopotentials which I owe to V. Heine.

Yes, Virginia, contrary to the conventional wisdom, there is a theory of high T_c superconductivity which gives a highly satisfactory explanation of most of the facts which are facts, though it is not exactly what you have been hearing. But it is as long, deep and devious as a physical theory can be, and I here relate a couple of parts of it which are related to the theory of pseudopotentials, which I learned from Volker and his friends and collaborators.

There are two places where pseudopotentials play an all-important role in the theory of high T_c: in the understanding of the parameters of the Hubbard model which underlies the whole phenomenon; and in the understanding of the divergence which, to our surprise and delight, invalidates the use of Fermi liquid theory to describe the metallic state in this model.

I will not bore you with the well-known structures of these materials, which in any case you have already seen. The operative elements are the CuO_2 planes (see figure 1), which can occur with or without the apical oxygens which complete an irregular pyramid or octahedron of O about each Cu. Aside from being good indicators of the electronic structure on the Cu, these are not electronically relevant.

All of the interesting action, in fact, takes place in the rather strongly bonding σ-bands of the CuO_2 structure. The π bands are entirely full at the physical occupancy, and do not contribute to bonding; so one is left with d_z^2 and $d_{x^2-y^2}$ orbitals on the Cu – with a slight but NMR-relevant admixture of Cu4s – and p_σ on the oxygen.

The 'chemical pseudopotential' method which Dave Bullett and I originated some years ago is the simplest way of setting up an effective hamiltonian for the relevant bands. If you remember, the idea was to rely on the chemical observation that in compounds like this with relatively large interband gaps, LCAO theory gives a good

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qualitative account, and what the chemists call ‘extended Hückel’ even a quantitative one, of the electronic structure. We search for the best atomic-like orbitals by using non-orthogonal orbitals and pseudizing away the biggest part of the effects of the neighbouring atoms. We have two systems of equations, a pseudopotential equation for the atomic orbitals and a derived effective ‘Hückel’ type hamiltonian for the actual energy levels.

In the present case, there’s a detail which must be taken care of: we must somehow make a hole–particle transformation because we are interested only in the top of the band: in how extra holes repel each other rather than extra electrons. For holes, atom cores represent strong repulsive hard cores, but as far as I can see pseudization can be used to mitigate the effects of hard cores just as well; this was in fact the original use of pseudopotentials.

If we look at the band upside down, in this way, we realize that it is not at all interesting to include the bonding orbitals, which are simply part of a lot of high-energy junk taking maximum advantage of the (now repulsive) ion cores. There is no way that they could, in some esoteric fashion, contribute to an effective attraction between holes: all of the nonsense about ‘extended Hubbard models’ just drops away. What is left is to solve for the antibonding pseudo-Wannier functions of $\mathrm{Cu}_{x^2-y^2}$ and Cu_{z^2} symmetry, and to study the shift in their energies as we vary the occupancy from zero to one to two holes. Dave Bullett has developed a kind of two-stage version of this procedure: first we set up non-orthogonal atomic orbitals which give the parameters of an effective hamiltonian by

$$(T+V_{\mathrm{Cu}})\varphi_{\mathrm{Cu}}-\sum_{\mathrm{O}}[(\varphi_{\mathrm{O}}|V_{\mathrm{O}}|\varphi_{\mathrm{Cu}})\varphi_{\mathrm{O}}-V_{\mathrm{O}}\varphi_{\mathrm{Cu}}]=E_{\mathrm{Cu}}\varphi_{\mathrm{Cu}},$$

$$(T+V_{\mathrm{O}})\varphi_{\mathrm{O}}-\sum_{\mathrm{Cu}}[\varphi_{\mathrm{Cu}}|V_{\mathrm{Cu}}|\varphi_{\mathrm{O}})\varphi_{\mathrm{Cu}}-V_{\mathrm{Cu}}\varphi_{\mathrm{O}}]=E_{\mathrm{O}}\varphi_{\mathrm{O}},$$

and $$\mathscr{H}_{\mathrm{O-Cu}}=\int\varphi_{\mathrm{Cu}}\,V_{\mathrm{Cu}}\varphi_{\mathrm{O}}\,\mathrm{d}^3r,\quad \mathscr{H}_{\mathrm{Cu-O}}=\int\varphi_{\mathrm{O}}\,V_{\mathrm{O}}\varphi_{\mathrm{Cu}}\,\mathrm{d}^3r.$$

(Note the simplifying difference in the way the bonding matrix elements are calculated.)

Then we set up, using these parameters, a pseudo-Wannier bonding or antibonding function which, again, need not be orthogonalized, and rather approximately (but the corrections can be calculated simply) is an eigenfunction of the ‘cluster’ hamiltonian of a Cu and its neighbour oxygens:

$$\Psi^{\mathrm{PW}}_{\mathrm{hole}}=\alpha\varphi^{x^2-y^2}_{\mathrm{Cu}}-\beta\sum_{1}^{4}\varphi^{\mathrm{p}^{\sigma}}_{\mathrm{O}i}(-1)^i.$$

I obviously neither have, nor am going to, explicitly do calculations for this system: much more able people, like Michael Schluter or Dave Bullett, have done them for me. But it is very interesting to think about where the parameter ‘U’ comes from. Although the above is a one-electron calculation, what we can do is to repeat the local one-electron calculation for two different local occupancies.

This then becomes virtually identical to the kind of local cluster theory which George Sawatsky or Jim Allen use to understand PES results or to Gunnarson’s LCI theory. If we, for instance, are calculating for the first hole to be removed from the cluster, the Cu d level is high (attractive for holes), about 3–4 eV above the $\mathrm{O_{2p}}$ level.

The net result is an energy level which is dominantly Cu $d_{x^2-y^2}$, not strongly antibonding but somewhat (since V_{pd} is only about comparable with the p–d splitting).

Removing one of these electrons, the next electron sees a Cu d level lower than the oxygen (but not much lower, since the electron came *ca.* 30% from oxygen) and we get an antibonding level which is somewhat more O than Cu; the difference is, effectively, 'U', which is then never bigger than the smaller Cu–O splitting, since the electron can at worst simply shift from Cu to O. But it is important to realize that these are not orthogonal d and p orbitals, and that even a pure d or p level still has some bonding character: the Jahn–Teller bond still has considerable strength even in the nominally purely ionic system. Thus the shift in atomic provenance does not mean that the electrons are from different bands, as is often mistakenly assumed.

A much more interesting and, as yet, controversial use of the pseudopotential concept and of all the experience with scattering wave functions and phase shifts which we garnered in the 1960s, is in the central proof of the non-Fermi liquid character of the two-dimensional Hubbard model. In fact, I would stick my neck out and say that no single-band interacting Fermi system in two dimensions is a Landau–Fermi liquid.

One of the most disturbing things about this pesky subject is the way it has of destroying prejudices which we all seem to have unconsciously enshrined as facts, over the years. I cribbed from Joseph Ford via James Gleick's book a marvellous quotation from Tolstoy on this subject:

> I know that most men... can seldom accept even the... most obvious truths, if they be such as would oblige them to admit the falsity of conclusions which they have delighted in explaining to colleagues, which they have proudly taught to others, and which they have woven... into the fabric of their lives.

Just such a prejudice is that the Landau theory is derived from many-body perturbation theory, which is fundamental and exact.

In a sense, Landau theory can be the more fundamental, since it can be derived from a consistent renormalization group procedure, while the perturbation theory is incomplete because, as normally carried out, it does not contain within itself the proper determination of the particle–particle scattering vertex which it uses in the Hartree terms which begin the series. I will save for later the first of these thoughts, and only talk here about the determination of the pseudopotential for particle–particle interaction.

This is, of course, a very old problem extending back into the history of many-body theory. Brueckner got his name on the idea that hard core interactions had to be renormalized away by replacing the simple interaction $V_{kk'}$ by an effective interaction for which he proposed the use of the scattering matrix $T_{kk'} = V_{kk'} + (VG_0V)_{kk'} + \dots$ Lee, Yang and Huang gave a fairly rigorous treatment of this process in the low-density limit, and seemed to convincingly show that an 'effective scattering length' theory was the appropriate solution. The meaning of this resummation is the observation that in the actual region where two particles are close to each other, unless the interactions are very long-range indeed it is never valid to assume that the wave-functions are unperturbed, and so one must in some sense solve a local Schrödinger equation for the scattering states, to get the correct asymptotic behaviour of the wave-functions. In a sense, every pair of particles experiences a Jastrow-like 'hole' in the near region. Where everything behaves

Figure 1

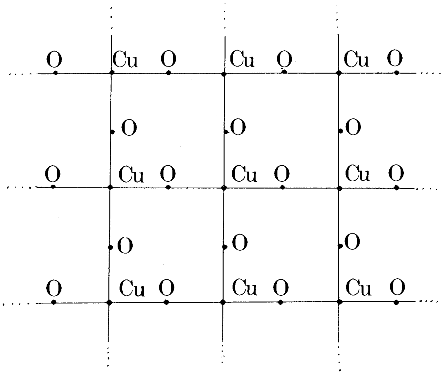

Figure 2

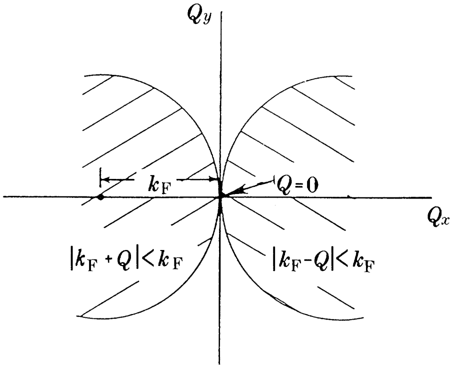

Figure 1. CuO_2 lattice.
Figure 2. Region of recoil momentum Q excluded by the Pauli principle.

regularly, as in three dimensions and for moderate interactions and free-electron bands, for two particles with relative momentum Q

$$T = (e^{i\eta}\sin\eta)/Q \sim \eta/Q$$

for small Q and phase-shift. The phase shift η is Qa, where a is the scattering length, so V is replaced by a finite, simple pseudopotential which merely expresses the fact that there is an additional kinetic energy caused by the small restriction on Hilbert space due to the atom cores. If this is the case, everything remains finite and Fermi liquid theory works. In particular, any one particle k does not cause an appreciable scattering phase shift for any other particle k', and it is consistent to treat the quasiparticles as though they occupied exactly the same volume in Hilbert space as the corresponding free electron gas. (The actual shift is *ca.* a/L where L is the sample size.) It is important, however, to realize that when we solve the scattering Schrödinger equation to get the local wave function, we are always doing so in the presence of boundary conditions: we are no longer dealing just with free plane waves but either with real standing waves $\sin(kr)$, $\cos(kr)$, or with ingoing and outgoing partial waves. Thus the naive picture of a Hartree term as just a $q = 0$ scattering is now false, and it includes both forward and backward scattering.

Not long thereafter Bloom took a look at the same problem in one and two dimensions, and discovered that the situation was by no means as simple in the low density limit (which is, I repeat, the only limit where rigorous results exist). In fact, in this limit the scattering length diverges, in one dimension like the sample size L and in two dimensions like $L/\ln L$, so that in the limit $Q \rightarrow 0$, $\eta_{1D} = \pi$ and $\eta_{2D} \sim 1/\ln L$. This means that the wave-function correction extends throughout the sample in one dimension since, after all, any scattering at all effectively changes the boundary conditions in one dimension and halves the effective length of the sample. Correspondingly, there are no Fermi liquids in one dimension, even for weak repulsive forces.

In two dimensions, the problem of the T-matrix becomes quite tricky. The phase shift, however, tends to 0 as $1/\ln L$, and Galitskii showed that in that case a Fermi liquid theory can indeed be made to – barely – converge.

These problems in one and two dimensions have to do with, not the short-range part of the solution of the Schrödinger equation, but the long-range part: the behaviour 'on the energy shell' which was always a thorn in the side of the multiple-scattering theory. In solving the T-matrix equation $T = V + VG_0 T$ or $T = (1-VG_0)^{-1}V$, one has to worry in detail about what happens at the pole in G_0 corresponding to the state actually being considered, or, specifically, what boundary conditions do you apply? (Again, boundary conditions!) Another way of seeing the problem is to look at the low-momentum solutions to scattering theory, and realize that these are simply $(x-a)$ in one dimension and $\ln r/a$ in two, both of which have relevant long-range as well as short-range behaviour.

What I discovered, and what actually is really terribly obvious, is that in two dimensions, for a cut-off band or in the Hubbard model, the Galitskii calculation becomes even more singular when one takes the exclusion principle into account. In effect, the phase-shift for zero density vanishes because the particles can recoil with any low energy: but if there is a filled Fermi sea, these low-energy recoils are excluded, the long-range part of the $\ln r/a$ wave-function is cut off, and the result is a finite phase shift, caused by the resulting finite logarithmic derivative of the relative wave-function.

The way of showing this is very easy, if one recognizes the vital role of boundary conditions and the energy shell. The relevant calculation is that of the actual energy shift of two particles with zero relative momentum, presuming that the two particles are near the Fermi surface, i.e. in the $K_{\text{tot}} = 2k_{\text{F}}$ singlet particle–particle channel. If we wish to calculate the energy shift, we must, of course, occupy the two relevant states, but we cannot allow them to recoil into states already occupied by other electrons, because of the exclusion principle. The equation which we must satisfy, then, is if we let

$$E_Q = \epsilon_{k+Q} + \epsilon_{k-Q}$$

and

$$\Psi_{\text{scatt}} = \sum_{Q} a_Q\, c^+_{k+Q\uparrow}\, c^+_{k-Q\downarrow}\,|0\rangle,$$

is

$$\mathscr{H}\Psi_{\text{scatt}} = E\Psi_{\text{scatt}} = \frac{U}{L^2}\sum_{QQ'} a_Q\, c^+_{k+Q'\uparrow}\, c^+_{k-Q'\downarrow} + \sum_{Q} E_Q\, a_Q\, c^+_{k+Q\uparrow}\, c^+_{k-Q\downarrow},$$

or

$$(E-E_Q)\,a_Q = \frac{U}{L^2}\sum_{Q} a_{Q'}, \qquad 1 = \frac{U}{L^2}\sum_{Q'}\frac{1}{E-E_{Q'}}.$$

If there is no exclusion principle, life is simple. In two dimensions, near the bottom of the band, states are evenly spaced,

$$E_Q = E_0 + Q^2, \quad (Q = n_x\pi/L,\, n_y\pi/L).$$

The lowest eigenvalue lies near E_0 so we have

$$\frac{1}{E-E_0} = \frac{L^2}{U} + \sum_{Q=\pi/L}^{Q_{\max}} \frac{1}{Q^2-E} = \frac{L^2}{U} + \frac{L^2}{\pi^2}\ln\frac{L}{a}$$

and, as Bloom found, $(E-E_0)/(E_1-E_0) \approx 1/(\ln La^{-1})$. Thus asymptotically, the energy in the relative motion must be slightly higher, and in the scattered wave function there is a small shift in Q, but this vanishes as $L \rightarrow \infty$.

Now consider the case where there is a finite density, $k_{\text{F}} > 0$. Now, if Fermi liquid theory were correct, the states $k+Q$ will be occupied with density $n_{\text{F}}(\epsilon_{k+Q})$ which (see figure 2) will exclude recoils in all but a narrow band of final states of density $Q^2/\pi k_{\text{F}}^2$. In essence, the wave function of relative motion $\ln r/a$ contains, in its longer-range parts, momenta which are not available because already occupied. Fortunately, because of the exclusion principle the sum no longer depends in detail on the low-energy end so that the treatment of Qs near zero is unimportant; and we simply remark that the exclusion principle cuts off the logarithm at k_F, not π/L:

$$\frac{\delta E}{\text{spacing}} = \frac{E-E_0}{E_1-E_0} \sim \frac{1}{\ln (k_F a)} \sim \eta_{l=0}.$$

The phase-shift as $Q \rightarrow 0$ is finite! Thus the same difficulties which prevent the validity of FLT in one dimension are completely valid here.

It is not appropriate here to go into too great detail as to what this does to the ground-state wave function.

What we can be sure of is that the two-dimensional Hubbard model has no normal state which is a Fermi liquid, even for low density or weak coupling and *a fortiori* for strong coupling and high density as in the CuO_2 planes. How this fact leads to the rest of the phenomenology of high T_c superconductivity is pretty well understood, but lengthy; and this meeting is not about that. I do believe that this is a generalizable statement which applies as well to SDW and CDW-forming systems like $NbSe_2$ and TaS_2, surface bands on semiconductors, or quasi-two-dimensional organics: we will just have to face the fact that we must rethink the physics of all of these restricted dimensionality systems, sometime quite soon. I hardly need to tell Volker, of course, that the conventional 'nesting Fermi surface' ideas never really carried plausibility to properly observant theorists.

With these disturbing but exciting thoughts I shall close. TCM, as a subject, is alive and not just well but kicking; to mix metaphors, the cat has not only not got all the cream, we seem to have tapped into a wholly new and unexpected set of cows.

Discussion

J. N. Murrell (*University of Sussex, U.K.*). Is there a specific chemical feature of a single CuO_2 two-dimensional sheet that would lead to long-range electron pair correlation for HTSC structures? In my view the fact that these sheets are, in chemical terms, alternant systems systems (whose hamiltonian matrices can be blocked in the form

$$\begin{bmatrix} 0 & \boldsymbol{h} \\ \boldsymbol{h} & 0 \end{bmatrix}$$

may have significance, for the lowest eigenfunctions of such systems appear to have the electron correlation needed.

P. W. Anderson. (1) The bands do not have very good alternant symmetry because of O–O overlap effects. (2) In my opinion, supported by heuristics and by observations on one-layer Bi compounds, single layers are very interesting but not true superconductors. Elsewhere I have suggested that they are '$T_c = 0$ superconductors'. (3) The interesting region for superconductivity is large doping when the commensurability question ('nesting', 'spin gaps', etc., and ideas involving AB bonding between two sublattices) is no longer relevant.

T. M. Rice (*Zurich, Switzerland*). In a recent *Physical Review Letter*, Engelbrecht & Randeria examined the conventional perturbation theory of a low density repulsive Hubbard model and found that forward scattering did not invalidate Landau–Fermi liquid. How does this relate to Professor Anderson's work?

P. W. ANDERSON. We have been examining this paper, especially A. Georges and myself. The key point is that the problem occurs before perturbation theory, and cannot be found by resummation of the conventional diagrams assuming the vertex is not divergent, at least if the diagrams are done in the conventional way. The result can probably be demonstrated by calculating the Hartree self-energy shift accurately taking into account the detailed structure of Γ. In the conventional theory this term is calculated by a coupling constant integration rather than directly, but we now believe the theory is non-analytic in 'g' at every point. This integration is used, among other things, to avoid treating the behaviour of T on the energy shell (at the pole) in detail, which is what is necessary. Our view is that Randeria–Engelbrecht is simply irrelevant to the point.

The conventional theory, to put it another way, contains an infinite renormalization of the vertex due to recoil which is normally unexamined. Section 5 of AGD shows that each order of perturbation theory contains a correction to the assumed pseudo-potential a, the sum of which is a bit we have examined and found divergent.

V. HEINE (*Cambridge, U.K.*). Could Professor Anderson please comment on Hugenholtz's old problem, namely that perturbation theory for the electron gas cannot possibly converge in one, two or three dimensions. The argument was that a power series has a circle of convergence, i.e. the same range of convergence for positive and negative interactions. Now an attractive Coulomb potential cannot give a convergent perturbation series and therefore the actual repulsive electron–electron interaction cannot give a convergent series either.

P. W. ANDERSON. This is a real problem for Fermi liquid theory, discussed at length in AGD, §12. Fortunately, for repulsive forces the Cooper singularity renormalizes the $k, -k$ scattering to zero; this renormalization is non-analytic but *improves* convergence. It does lie outside naive perturbation theory.