One-electron bands, quantum Monte Carlo, and real superconductors

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\textbf{Abstract}

We use the doped Fullerenes as an example of how realistic systems can be described by simple models. Starting from the band structure we set up a tight-binding model that describes the $t_{1u}$ conduction band. Adding correlation terms we arrive at a generalized Hubbard Hamiltonian that we treat using quantum Monte Carlo. To address the problem of superconductivity in the doped Fullerenes, we study the screening of a point charge. We find surprisingly efficient metallic screening even for strong correlations, almost up to the Mott transition, and discuss the implications on superconductivity, in particular the effect of the efficient screening on the Coulomb pseudopotential and the electron-phonon coupling.

\textit{Key words:} superconductivity, Coulomb pseudopotential, electron-phonon coupling, Hubbard model, orbital degeneracy, Fullerenes, quantum Monte Carlo

\textit{PACS:} 74.70.Wz — 71.10.Fd

\textbf{1 Introduction}

The sheer size of the many-body Hilbert space makes treating strongly correlated systems adequately extremely difficult or even impossible. Examples of considerable interest are the superconducting doped Fullerenes. Even for a single C\textsubscript{60} molecule a full many-body calculation is still a challenge and calculations for solids made of Fullerenes are simply out of question. In this situation we are forced to restrict our attention to only the most relevant degrees of freedom. For the doped Fullerenes these are the electrons in the $t_{1u}$-band. Starting from \textit{ab initio} density functional calculations we set up a tight-binding Hamiltonian that describes the electrons in the $t_{1u}$-band only.

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Including correlation effects we arrive at a generalized Hubbard Hamiltonian that can be treated by quantum Monte Carlo (QMC). Using the fixed-node approximation we study the screening of an point charge by the electrons in the $t_{1u}$-band. We find that the screening is surprisingly efficient even for strong correlations, almost up to the Mott transition. This has important implications for superconductivity in the doped Fullerenes. Given that molecular vibration energies are of the same order as electronic energies, retardation effects are inefficient at reducing the electron-electron repulsion. It is therefore not clear how the weak electron-phonon attraction can lead to superconductivity. Efficient metallic screening, as found in our calculations, can, however, reduce the electron-electron repulsion enough to allow for an electron-phonon driven superconductivity. But the screening does, of course, also affect the coupling to the phonons. It turns out that, due to screening, the alkali and $A_g$ modes couple only weakly, while the coupling to the $H_g$ modes is not affected. Therefore, although being electron-phonon driven, superconductivity in the doped Fullerenes differs in important ways from the conventional picture of superconductivity.

2 Model Hamiltonian

Treating correlations in the Fullerenes is quite difficult. Even for a single $C_{60}$ molecule a full many-body calculation is still a challenge and simulations of Fullerenes, which are solids made of $C_{60}$ molecules are well beyond current computational capabilities. Solid $C_{60}$ is characterized by weak inter-molecular interactions. Hence the molecular levels merely broaden into narrow, well-separated bands [1]. Doping the solid with alkali metals has the effect of filling the band originating from the molecular $t_{1u}$-level with the weakly bound valence electrons of the alkali atoms. Since the $t_{1u}$-level is three-fold degenerate the corresponding band can hold up to six electrons per molecule; for $A_3C_{60}$, e.g., the band is half-filled. When we are interested in the low-energy properties of the $t_{1u}$ electrons, it is a good approximation to focus only on the region around the Fermi level; i.e. on the $t_{1u}$-band, projecting out all the other bands [2]. That way we arrive at a tight-binding Hamiltonian comprising only the $t_{1u}$ orbitals, that reproduces the ab initio band structure remarkably well [3].

To obtain a realistic description we have to include the correlation arising from the Coulomb repulsion among the electrons on the same molecule. The resulting Hamiltonian describes the interplay between the hopping of electrons between different molecules and the Coulomb repulsion among the electrons on the same molecule

$$H = \sum_{\langle ij \rangle} \sum_{nn'\sigma} t_{in,jn'} c_{in\sigma}^\dagger c_{jn'\sigma} + U \sum_{i} \sum_{\langle n\sigma \rangle < \langle n'\sigma' \rangle} n_{in\sigma} n_{in'\sigma'}.$$  \hfill (1)
Here $c_{in\sigma}^\dagger$ creates an electron of spin $\sigma$ in the orbital with index $n \in \{1, \ldots, 3\}$ on molecule $i$, the $t_{in,jn}$ are hopping matrix elements between orbitals $n$ and $n'$ on neighboring molecules, and $n_{in\sigma} = c_{in\sigma}^\dagger c_{in\sigma}$ are occupation operators. Varying the value of the interaction term $U$, we can study the effect of correlations. The physical value for the doped Fullerenes is $U \approx 1.2 - 1.4$ eV [4], which has to be compared to the width of the $t_{1u}$-band, $W \approx 0.5 - 0.85$ eV.

3 Quantum Monte Carlo

We now give a very brief outline of the quantum Monte Carlo method for determining ground states. The basic idea is to use the Hamiltonian to project out the ground-state from some trial function $|\Psi_T\rangle$, that we have guessed:

$$e^{-\tau H} |\Psi_T\rangle \xrightarrow{\tau \to \infty} |\Psi_0\rangle. \quad (2)$$

To see how this works let us assume we knew the expansion of the trial function in eigenfunctions of $H$

$$|\Psi_T\rangle = \sum_n c_n |\Psi_n\rangle \Rightarrow e^{-\tau H} |\Psi_T\rangle = \sum_n c_n e^{-\tau E_i} |\Psi_n\rangle. \quad (3)$$

Thus the component with the lowest eigenenergy is damped least during the projection, i.e., if $c_0 \neq 0$, in the limit of large $\tau$ the ground-state component will dominate. In practice we use for Hamiltonians $H$ with a spectrum that is bounded, both, from below and above, an iterative projection of the form [5]

$$|\Psi^{(0)}\rangle = |\Psi_T\rangle \quad |\Psi^{(n)}\rangle = [1 - \tau(H - E_0)]|\Psi^{(n-1)}\rangle, \quad (4)$$

which, for small but finite $\tau$, also exactly projects to the ground-state. We see that the basic operation in (4) is a matrix-vector product. Since we are working in a many-body Hilbert space, the dimension of the vectors is, however, in general enormous; see Table 1 for an illustration.

To understand the Monte Carlo method for doing the iteration we first rewrite (4) in configuration space. Here $R$ denotes a configuration of the electrons in real space

$$\sum_{R,R'} |R\rangle \langle R'| |\Psi^{(n)}\rangle = \sum_{R,R'} |R\rangle \langle R'| [1 - \tau(H - E_0)]|R\rangle \langle R| |\Psi^{(n-1)}\rangle =: F(R', R). \quad (5)$$

We see that the matrix $F(R', R)$ maps configuration $R$ into configurations $R'$. We clearly cannot follow every possible new configuration $R'$ since that
\[ \begin{array}{c|ccc}
N_{\text{mol}} & \text{dimension} & \text{memory/GB} \\
\hline
4 & 853 776 = 8.5 \cdot 10^5 & 3.2 \cdot 10^{-3} \\
8 & 7 312 459 672 336 = 7.3 \cdot 10^{12} & 2.7 \cdot 10^4 \\
16 & 1.0 \cdot 10^{27} & 3.9 \cdot 10^{18} \\
32 & 4.1 \cdot 10^{55} & 1.5 \cdot 10^{47} \\
64 & 1.3 \cdot 10^{113} & 4.9 \cdot 10^{104} \\
108 & 2.3 \cdot 10^{192} & 8.5 \cdot 10^{183} \\
\end{array} \]

Table 1
Dimension of the Hilbert space for a system with \( N_\uparrow + N_\downarrow \) electrons on \( M \) lattice sites. For our model of doped Fullerenes \( M = 3 N_{\text{mol}} \). The last column gives the amount of memory needed to store a single state vector.

would lead to an exponential growth in the number of configurations as we iterate. The idea of Monte Carlo is then to sample only one of the configurations \( R' \) with a probability \( p(R', R) \). To do that we want to interpret the matrix elements of \( F(R', R) \) as probabilities. They are, however, in general not normalized and can even be negative

\[
F(R', R) = p(R', R) \cdot m(R', R).
\]

Normalization introduces the need for population control, while negative matrix elements introduce the sign problem [6,7].

4 Screening of a Point Charge

In conventional superconductors the electron-phonon interaction leads to an effective electron-electron attraction. This attraction is, of course, counteracted by the Coulomb repulsion between the electrons. In the conventional picture this repulsion is, however, strongly reduced by retardation effects [8]. The resulting effective Coulomb repulsion is described by the dimensionless Coulomb pseudopotential \( \mu^* \), which is believed to be of the order of 0.1. For the doped Fullerenes the situation is different: Retardation effects are inefficient [9]. Therefore the screening of the Coulomb interaction becomes important for reducing the electron-electron repulsion. Assuming that the random phase approximation (RPA) is valid for the electrons within the \( t_{1u} \)-band it was found that efficient metallic screening significantly reduces the Coulomb pseudopotential [10]. In this scenario the Coulomb pseudopotential \( \mu^* \approx 0.3 \) is substantially larger than that for conventional superconductors, but it is not too large to prevent superconductivity from being driven by the electron-phonon interaction. For strongly correlated systems like the doped Fullerenes
the use of the RPA seems, however, highly questionable.

To address this question, we have investigated how well the RPA describes the screening within the $t_{1u}$-band. It is clear that the RPA properly describes the screening when the kinetic energy is much larger than the interaction energy, i.e. RPA works well in the weakly correlated limit. For strong correlations, where the Coulomb energy dominates, the RPA gives qualitatively wrong results: Introducing a test charge $q$ on a molecule, RPA predicts that almost the same amount of electronic charge moves away from that molecule, since for a Coulomb integral $U$ much larger than the bandwidth $W$ the gain in potential energy dominates the cost in kinetic energy. The RPA neglects, however, that in this limit, when an electron leaves a molecule it has to find another molecule with a missing electron, or there will be a large increase in Coulomb energy. It is not clear for what value of the Coulomb interaction $U$ this qualitative breakdown of the RPA starts, and up to which values of $U$ RPA gives still accurate results. To find out we have performed quantum Monte Carlo calculations. To study the screening of a point charge $q$ on molecule with index $c$ we consider the Hamiltonian

$$H = \sum_{\langle ij \rangle} \sum_{nn'\sigma} t_{in,jn'} c_i^{\dagger} c_{jn'}^{\sigma} + U \sum_{i} \sum_{\langle n\sigma \rangle < \langle n'\sigma' \rangle} n_{in\sigma} n_{in'\sigma'} + qU \sum_{n\sigma} n_{cn\sigma},$$

(7)

which differs from (1) only by the last term describing the interaction with the test charge. As a trial function we use a generalized Gutzwiller function of the form

$$|\Psi_T\rangle = g^D g_0^{n_c} |\Phi_0\rangle,$$

(8)

where $|\Phi_0\rangle$ is a Slater determinant, $D$ is the number of double occupancies in the system, and $n_c$ is the number of electrons on the molecule with the test charge. Calculating the expectation value $n_c(VMC) = \langle \Psi_T | n_c | \Psi_T \rangle$ by variational Monte Carlo and the mixed estimator $n_c(DMC) = \langle \Psi_T | n_c | \Psi_0 \rangle$ by fixed-node diffusion Monte Carlo, we obtain the ground-state expectation value $n_c = \langle \Psi_0 | n_c | \Psi_0 \rangle$ from the extrapolated estimator $n_c \approx 2n_c(DMC) - n_c(VMC)$. To estimate the accuracy of our approach we have compared the results of the quantum Monte Carlo (QMC) calculations with the results from exact diagonalization for a cluster of 4 molecules. We find that the QMC calculations are accurate up to very large values of the Coulomb interaction $U$. Performing QMC calculations for clusters of sizes $N_{mol} = 32, 48, 64, 72,$ and 108 molecules, where exact diagonalization is not possible (cf. Table 1), we have extrapolated the screening charge $\Delta n_c = n_c(0) - n_c(q)$ to infinite cluster-size, assuming a finite-size scaling of the form $\Delta n_c = \Delta n_c(N_{mol}) + \alpha/N_{mol}$ [11]. The finite-size extrapolation gives only a small correction to the screening charge found for the larger clusters. Results for $q = 0.25 e$ are shown in Figure
Fig. 1. Screening charge $\Delta n$ on the site of a test charge $q = 1/4$ electron charges as a function of $U/W$, extrapolated to infinite cluster size.

1. For small values of $U$ the RPA somewhat underestimates the screening, a behavior also found in the electron gas [12]. For intermediate values of $U$ ($U/W \approx 1.0 - 2.0$) the RPA still gives surprisingly accurate results, while for larger $U$ it rapidly becomes qualitatively wrong, as discussed above. We thus find efficient, RPA-like screening even for quite strong correlations close to the Mott transition.

5 Screening and Electron-Phonon Coupling

As pointed out in the preceding discussion, efficient metallic screening helps to reduce the effective electron-electron repulsion, i.e. the Coulomb pseudopotential. But the screening also affects the electron-phonon coupling. At first it might appear that efficient screening is not really helpful for superconductivity. Phonons couple to the electrons by perturbing the potential seen by the electrons. An example is the longitudinal mode of a jellium. Efficient screening tends to weaken the coupling to such phonons, since it reduces the perturbation considerably: The bare coupling constant $g$ is reduced to $g/\varepsilon$, where $\varepsilon$ is the dielectric constant [8]. To some extent, such a reduction is also at work in the Fullerenes. An example are the alkali phonons. Each $C_{60}$ molecule is surrounded by 14 alkali ions that are bound with quite weak force constants. They should therefore respond strongly when an electron arrives on a $C_{60}$ molecule. This was, however, not confirmed experimentally; an alkali isotope effect could, e.g., not be observed [13]. Given the efficient metallic screening this finding can be naturally understood. When an electron arrives on a $C_{60}$ molecule, other electrons leave the molecule, which thus stays almost neutral.
Fig. 2. Schematic picture of the change in the energy levels as function of the phonon coordinate $Q$ (deformation of molecule). The left picture shows a phonon that shifts the center of gravity of the energy levels, while in the right picture the center of gravity is conserved.

The alkali ions then see only a small change in the net charge and therefore couple weakly.

To analyze the situation more closely, we consider the change in the energy of the molecular orbital $\alpha$ under a deformation of the molecule with amplitude $Q$

$$
\Delta \varepsilon_\alpha^0 = g_\alpha Q,
$$

where $g_\alpha$ is the electron-phonon coupling. An illustration is given in Figure 2. The change of the on-site energy $\varepsilon_\alpha^0$ will induce a response of the $t_{1u}$ electrons. Since the effect of a point charge $q$ is just to shift the on-site energy by $q U$ (cf. (7)), the screening charge induced by the change $\Delta \varepsilon_\alpha^0$ is given by

$$
\Delta n_\alpha = -\gamma \frac{\Delta \varepsilon_\alpha^0}{U},
$$

where $\gamma > 0$ measures the efficiency of the screening: $\Delta n = -\gamma q$. The total screening charge induced by the molecular deformation $Q$ is then given by

$$
\Delta n = \sum_\alpha \Delta n_\alpha = -\frac{\gamma}{U} \left( \sum g_\alpha \right) Q.
$$

Including screening, the shift in the molecular levels is then given by

$$
\Delta \varepsilon_\alpha = \Delta \varepsilon_\alpha^0 + U \sum_\beta \Delta n_\beta = \left( g_\alpha - \gamma \sum_\beta g_\beta \right) Q.
$$

For molecular solids like the doped Fullerenes the electron-phonon coupling is given by the dimensionless constant [14]

$$
\lambda \propto \sum_\alpha \left( \frac{\Delta \varepsilon_\alpha}{Q} \right)^2 = \sum_\alpha \left( g_\alpha - \gamma \sum_\beta g_\beta \right)^2.
$$
Given efficient metallic screening ($\gamma \approx 1$), the coupling to phonons that cause a net shift of the molecular levels $\sum g_\beta \neq 0$ will be reduced, while modes that leave the center of gravity of the molecular levels unchanged ($\sum g_\beta = 0$) will not be affected. Such modes are the $H_g$ modes in $C_{60}$. For these modes efficient screening serves to reduce the electron-electron repulsion without affecting the electron-phonon coupling.

6 Conclusion

We have described how to construct a model for the $t_{1u}$ electrons in the doped Fullerenes, that can be analyzed by many body techniques. Using quantum Monte Carlo we have calculated the static screening of a point charge. We find that the RPA works surprisingly well, almost up to the Mott transition. The metallic screening helps to reduce the electron-electron repulsion in the doped Fullerenes, where retardation effects are inefficient. But the screening in general also reduces the electron-phonon coupling. In a molecular solid there can be, however, intra-molecular modes that are not screened, examples being the $H_g$ modes in the Fullerenes. We thus find that, although superconductivity in the Fullerenes is driven by the electron-phonon coupling, it differs in important points from the textbook picture of superconductivity.

Acknowledgements

This work has been supported by the Alexander-von-Humboldt-Stiftung under the Feodor-Lynen-Program and the Max-Planck-Forschungspreis.

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