Strongly correlated electrons: Estimates of model parameters

Why model Hamiltonians?

Simple example. Intuitive approach.

Applications: $3d$, $4f$ and $C_{60}$ compounds.

What is left out?

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Density functional formalism

\[ \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + u_{xc}(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \]

If good approximation to \( u_{xc} \) known, tremendous simplification.

1. Effective, local one-particle potential.
2. Efficient numerical methods available.
3. Used in large majority of *ab initio* solid-state physics calculations.
4. Surprisingly successful.

But

1. No systematic procedure for improving approximations for \( u_{xc} \). For strongly correlated systems, LDA and GGA often not good enough.
2. In principle only ground-state properties. \( \varepsilon_i \) often (successfully) treated as excitation energies. But even if exact \( u_{xc} \) known, \( \varepsilon_i \) in general *not* an exact excitation energy (But time-dependent DFT).

Need for many-body theory.
GW approximation

Based on diagrammatic theory.

\[ \Sigma = \int W \]

\( G_0 = \) Zeroth order Green’s function.

\( W = \) Screened interaction.

Simplest diagram in an expansion in \( W \).

Dyson’s equation: \( G = G_0 + G_0 \Sigma G \).

Improves LDA (or GGA) for semiconductors.

But not sufficient for strongly correlated systems.

More complicated diagrams can be calculated, but hard to choose diagrams. No systematic expansion.

Alternative: Find (simple) model which can be solved accurately.
Model calculations

1. Often large systems: $\text{YBa}_2\text{Cu}_3\text{O}_7$ (13 atoms); $\text{K}_3\text{C}_6\text{O}_{10}$ (60 atoms).

2. Correlation effects important: Often close to Mott transition. Often $3d$ or $4f$ compound.

3. LDA(GGA) cannot address many of the interesting properties.

4. *Ab initio* quantum-chemical or many-body methods not feasible.

Often only model calculations possible.

Just keep strongest interactions and most important states.

Advantage: Easier to extract physics.

Danger: Use of oversimplified model, unrealistic parameters or too crude approximations in solving model.

Need to estimate parameters from *ab initio* calculations or experiments.
Ce. $\alpha - \gamma$ transition

Promotional model: $|\varepsilon_{4f} - E_F| < 0.1$ eV; $\Delta \sim 0.01$ eV.

Explains: $\alpha$-$\gamma$ - transition ($5d \rightarrow 4f$ trans.).

Explains: Large specific heat and susceptibility.

But: 1. $\varepsilon_{4f} - E_F \sim -2$ eV (Johansson, 1978). 2. $\tilde{\Delta} \sim 0.1$ eV.

Later:

Many-body effect produces narrow resonance at $E_F$.

Promotional model: Wrong parameters + simple (mean-field) solution appeared to give “correct” physics.
Hamiltonian

\[ H = \sum_i \left[ -\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{ext}}(r_i) \right] + \sum_{i<j} \frac{e^2}{|r_i - r_j|}. \]

Find some complete one-particle basis set.

\[ H = \sum_i \varepsilon_i n_i + \sum_{i \neq j} t_{ij} \psi_i^\dagger \psi_j + \frac{1}{2} \sum_{ijkl} v_{ijkl} \psi_i^\dagger \psi_j^\dagger \psi_l \psi_k. \]

This Hamiltonian can be solved for small atoms and molecules, using, e.g., quantum chemical methods. But it is too complicated for systems we have in mind here.

Need to

1) project out degrees of freedom

2) remove interaction terms
Hubbard model

E.g., consider just the $3d$ electrons in a transition metal (compound). Include Coulomb interaction between two electrons on same atom.

$$H = \sum_{ij} \sum_{\sigma} t_{i,j} \psi_{i\sigma}^{\dagger} \psi_{j'\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}.$$  

Anderson model

E.g., consider $3d$ impurity in $sp$ host. Include Coulomb interaction on impurity but not in host.

$$H = \sum_{k\sigma} \varepsilon_k \psi_{k\sigma}^{\dagger} \psi_{k\sigma} + \varepsilon_{3d} \sum_{\sigma} \psi_{\sigma}^{\dagger} \psi_{\sigma} + \sum_{k\sigma} V_k [\psi_{k\sigma}^{\dagger} \psi_{\sigma} + h.c.] + U n_{\uparrow} n_{\downarrow}.$$
Projecting out one-particle states

\[ H = \sum_i \varepsilon_i n_i + \sum_{i \neq j} t_{ij} \psi_i \psi_j. \]

Corresponding Hamiltonian matrix:

\[
\begin{pmatrix}
\varepsilon_1 & t_{12} & \cdots \\
t_{21} & \varepsilon_2 & \cdots \\
\cdots & \cdots & \cdots 
\end{pmatrix}
\]

\[
(z - H)^{-1} = \sum_{\nu} |\nu\rangle \langle \nu| (z - H)^{-1} \sum_{\mu} |\mu\rangle \langle \mu| = \sum_{\mu} |\mu\rangle \frac{1}{z - E_\mu} \langle \mu|.
\]

Resolvent operator has poles at eigenvalues \( E_\mu \).

Project out states Q and keep states P (Löwdin).

Hamiltonian matrix is rewritten in block form:

\[
\begin{pmatrix}
H_{PP} & H_{PQ} \\
H_{QP} & H_{QQ}
\end{pmatrix}
\]

Look for poles of smaller matrix

\[
[z - H_{PP} - H_{PQ}(z - H_{QQ})^{-1} H_{QP}]^{-1}.
\]

Identical to poles of \((z - H)^{-1}\) if eigenvectors have weight in P.
Projecting out one-particle states. Continuation

Look for the poles of the smaller matrix

\[ z - H_{PP} - H_{PQ}(z - H_{QQ})^{-1}H_{QP}\]^{-1}.\]

But matrix elements now energy dependent. Replace \(z\) by “typical” energy \(E_0\) in \((z - H_{QQ})^{-1}\). Study energy independent “small” Hamiltonian

This down-folding done efficiently in LMTO and provides hopping integrals for models.

Systematic and controlled approach.
Coulomb integrals: \[ F_{ij} = e^2 \int d^3r \int d^3r' \frac{\Phi_i^2(r)\Phi_j^2(r')}{|r-r'|}. \]

Mn: \( F_{3d,3d} \sim 21 \text{ eV}, \quad F_{3d,4s} \sim 10 \text{ eV}, \)
\( F_{nn} \sim 5 - 6 \text{ eV} \) (nearest neighbor).

Unjustified to keep \( F_{3d,3d} \) and neglect everything else. Furthermore \( F_{3d,3d} \sim 21 \text{ eV} \) is much too large to explain experiment.

Necessary to include neglected interactions implicitly as renormalization of parameters. (This reduces \( F_{3d,3d} \)).

What not included explicitly in model is (if possible) included implicitly as renormalization of parameters. What is included explicitly must not be included implicitly (double counting).

The values of the parameters depend on what model they are used in.
Empirical parameters depend on the property considered.
Many-particle problem

For one-particle problem project out higher states. Hopping more long-ranged and procedure accurate over a smaller energy range as more states are projected out, but procedure still controlled.

\[
H_{PP} - H_{PQ}(z - H_{QQ})^{-1}H_{QP}.
\]

For many-body problem not practical.

\(H\): Two-body operators with two creation + two annihilation operators.

\(Q\) projects out many-electron states with at least one electron in one-particle states to be projected out.

New terms with six operators. Very many terms.

We therefore rely on more intuitive and less rigorous approaches.
Simple model of 3d impurity

\[ H = \sum_{\sigma} \left[ \sum_{i=1}^{4} \varepsilon_i n_{i\sigma} + (t \psi_{1\sigma}^{\dagger} \psi_{2\sigma} + V \psi_{3\sigma}^{\dagger} \psi_{4\sigma} + h.c.) \right] + \]

\[ + U_{dd} n_{2\uparrow} n_{2\downarrow} + U_{sd} \sum_{\sigma\sigma'} n_{2\sigma} n_{4\sigma'}. \]

1. Orbital 2 very localized \( \Rightarrow t \) small.
2. Orbitals 3+4 delocalized \( \Rightarrow V \) large.

We want to project out dynamics of levels 3 and 4, assuming that electrons in space 3+4 can adjust perfectly to electrons in space 1+2.

Consider spinless case. Put the electron in space 1+2 on one level (1 or 2) and calculate the total energy.

\[ \varepsilon_1 = \varepsilon_2 \]
\[ \varepsilon_3 = \varepsilon_4 \]
\[ \varepsilon_{1\text{ eff}} = \varepsilon_1 + \varepsilon_{b1} \]
\[ \varepsilon_{2\text{ eff}} = \varepsilon_2 + \varepsilon_{b2}. \]
Simple model of 3d impurity

\[ H = \sum_\sigma [\sum_{i=1}^4 \varepsilon_i n_i \sigma + (t \psi_1^\dagger \psi_2 \sigma + V \psi_3^\dagger \psi_4 \sigma + h.c.)] + \]

\[ + U_{dd} n_{2\uparrow} n_{2\downarrow} + U_{sd} \sum_{\sigma\sigma'} n_{2\sigma} n_{4\sigma'}. \]

1. Orbital 2 very localized \( \Rightarrow t \) small.

2. Orbitals 3+4 delocalized \( \Rightarrow V \) large.

\[ \varepsilon_{1 \text{eff}} = \varepsilon_1 + \varepsilon_{b1}, \quad \varepsilon_{2 \text{eff}} = \varepsilon_2 + \varepsilon_{b2}. \]

\[ H_{\text{eff}} = \varepsilon_{1 \text{eff}} n_1 + \varepsilon_{2 \text{eff}} n_2 + t(\psi_1^\dagger \psi_2 + \psi_2^\dagger \psi_1). \]

\[ \varepsilon_{2 \text{eff}} - \varepsilon_{1 \text{eff}} = \frac{1}{2} U_{sd} - \frac{1}{8} \frac{U_{sd}^2}{V} + O\left(\frac{1}{V^2}\right). \]

Renormalized by less than \( U_{sd}/2 \), due to readjustments of charge.
Exact solution

Introduce complete basis set.

\[ |\tilde{1}\rangle = \psi_1^\dagger \psi_{b1}^\dagger |0\rangle, \quad |\tilde{2}\rangle = \psi_2^\dagger \psi_{b2}^\dagger |0\rangle \]

\[ |\tilde{3}\rangle = \psi_1^\dagger \psi_{a1}^\dagger |0\rangle, \quad |\tilde{4}\rangle = \psi_2^\dagger \psi_{a2}^\dagger |0\rangle. \]

Write down $4 \times 4$ Hamiltonian matrix. Project out states $|\tilde{3}\rangle$ and $|\tilde{4}\rangle$.

\[ \tilde{H}_{11} = \varepsilon_1 + \varepsilon_{b1} + \frac{t^2(z-\varepsilon_1-\varepsilon_{a1})\sin^2 \phi}{(z-\varepsilon_1-\varepsilon_{a1})(z-\varepsilon_2-\varepsilon_{a2})-t^2\cos^2 \phi}. \]

$\phi \sim U_{sd}/V$. Put $z \sim \varepsilon_1 + \varepsilon_{1b}$. Last term of order $t(t/V)(U_{sd}/V)^2$. For low energy properties:

\[ H^{eff} = \varepsilon_1^{eff} n_1 + \varepsilon_2^{eff} n_2 + t\cos \phi (\psi_1^\dagger \psi_2 + \psi_2^\dagger \psi_1) + O\left(\frac{1}{V^3}\right). \]

As elect. in 1+2 hops, elect. in 3+4 has to readjust. Hinders hopping.

To order $(U_{sd}/V)^2$, neglect $\cos \phi$ $\Rightarrow$ Simple effective Hamiltonian:

\[ H^{eff} = \varepsilon_1^{eff} n_1 + \varepsilon_2^{eff} n_2 + t(\psi_1^\dagger \psi_2 + \psi_2^\dagger \psi_1). \]

Spin degenerate model.

\[ H_{\text{eff}} = \sum_{\sigma} [\varepsilon_1^{\text{eff}} n_{1\sigma} + \varepsilon_2^{\text{eff}} n_{2\sigma} + t (\psi_{1\sigma}^+ \psi_{2\sigma} + \psi_{2\sigma}^+ \psi_{1\sigma})] + U_{\text{eff}} n_{1\uparrow} n_{1\downarrow}. \]

\[ U_{\text{eff}} = E(n_2=2) - E(n_2=0) - 2E(n=1). \]

\[ \varepsilon_2^{\text{eff}} - \varepsilon_1^{\text{eff}} = U_{sd} - \frac{1}{4} \frac{U_{sd}^2}{V} + O\left(\frac{1}{V^2}\right). \]

\[ U_{\text{eff}} = U - \frac{1}{2} \frac{U_{sd}^2}{V} + O\left(\frac{1}{V^2}\right). \]

<table>
<thead>
<tr>
<th>$V$</th>
<th>$\varepsilon_2^{\text{eff}} - \varepsilon_1^{\text{eff}}$</th>
<th>$U_{\text{eff}}$</th>
<th>$E_0 + 2V$</th>
<th>$n_2$</th>
<th>$\chi$</th>
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<tr>
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<td>Renorm.</td>
<td>Exact</td>
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Accurate for $V$ large. Two types of electrons.

Spin degenerate model.

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Two types of electrons?

In model of a 3d compound, we could renormalize out levels involving very delocalized electrons (hopping integrals large, electrons “fast”).

Can we separate electrons of real systems into localized and delocalized?

<table>
<thead>
<tr>
<th>System</th>
<th>Localized</th>
<th>Delocalized</th>
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<tbody>
<tr>
<td>$4f$ compounds</td>
<td>$4f$</td>
<td>$5d$</td>
</tr>
<tr>
<td>$3d$ compounds</td>
<td>$3d$</td>
<td>$4s, 4p$</td>
</tr>
</tbody>
</table>

Pretty good for $4f$ compounds ($W_{4f}/W_{5d} \sim 0.1$)

Questionable for $3d$ compounds, in particular at beginning of series.
Other high-lying excitations $A_3C_{60}$ ($A = \text{K, Rb}$)

Interesting physics in a partly occupied $t_{1u}$ band.

We want to project out other bands. This leads to important renormalization of $U$, due to important interband transitions, which are not explicitly included in effective model.

Add two electrons to one molecule. The surrounding molecules polarize. This reduces the energy cost.

The polarization is described by (fairly) high-energy interband transitions. These can be projected out and $U$ is renormalized.
“Perfect screening” (Herring)

Change occupancy of localized orbital \((3d, 4f)\).

Screening partly due to charge transfer to delocalized orbital on same atom \((4s, 5d)\).

Assume that screening is “perfect”, i.e., that atom stays neutral. Then calculation of \(U\) is reduced to (renormalized) atomic calculation.

\[
E(n_{4f}) = \frac{1}{2}Un_{4f}(n_{4f} - 1) + \varepsilon_{4f}n_{4f}.
\]

\[
U = E(5d^24f^{n+1}) + E(5d^44f^{n-1}) - 2E(5d^34f^n).
\]

E.g., Ce: \(U = E(5d^24f^2) + E(5d^44f^0) - 2E(5d^34f^1)\).

Calculations show that “perfect” screening is a good approximation for rare earths but not for transition metals.

Ce: 105% of screening inside the WS sphere.

Fe: 50% of screening inside the WS sphere (LMTO).
"Perfect" screening assumed.
"Renormalized" atom calculation (inside Wigner-Seitz sphere).

Exp.: Lang, Baer, Cox, PRL 42, 74 (1979).

But in general we cannot assume "perfect" screening.
Constrained density functional formalism

On-site Coulomb (Hubbard) interaction:

To estimate $U$ we need to know how the energy varies with the occupancy. This can be done by using a constrained DFT.

\[
E[n^i_{3d}] = F[n] + \int d^3r V_{ext}(r)n(r) + \mu\{\int d^3r n(r) - N\} \\
+ \mu^i_{3d}\{\int d^3r n^i_{3d}(r) - n^i_{3d}\}.
\]

Normally, we adjust $\mu$ so that number of electrons is $N$. Here we in addition adjust $\mu^i_{3d}$ so that number of $3d$ electrons on site $i$ is $N^i_{3d}$.

\[
0 = \frac{\partial F}{\partial n} + V_{ext}(r) + \mu + \mu^i_{3d}P^i_{3d}
\]

Results in constant potential $\mu^i_{3d}$ acting on $3d$ electrons on atom $i$.

\[
E(n_{3d}+1)-E(n_{3d}) \approx \varepsilon_{3d}(n_{3d} + 1/2)
\]

\[
U = E(n_{3d} + 1) + E(n_{3d} - 1) - 2E(n_{3d}) \approx \partial\varepsilon_{3d}/\partial n_{3d}.
\]

“Subtract the kinetic energy”

Changing $n_{3d}$ also changes kinetic energy. Straightforward application of constrained DFT incorrectly gives kinetic energy contribution to $U$.

Calculate $E[n^i_{3d}]$ in constrained mean-field theory for

$$H = \sum_{ij\sigma} t_{ij} \psi_i^\dagger \psi^i \sigma + \frac{1}{2} \sum_{ij\sigma\sigma'} U_{ij} n_{i\sigma} n_{j\sigma'}$$

Adjust $U_{ij}$ so that $E[n^i_{3d}]$ from constrained DFT reproduced.

Model and DFT give similar contribution from kinetic energy.

Hybertsen, Schlüter, Christensen, PRB 89, 9028 (1989).

Cococcioni, Gironcoli, PRB 71, 035105 (2005).
“Cut the hopping”

Remove the hopping integrals from localized orbital (LMTO).

1. We can easily vary the occupation number of the level by hand.

2. No hopping from the localized level to the surrounding, i.e., no (3d) kinetic energy contribution to $U$.

Practical approach:

1. Impurity program: Cut hopping to localized level on impurity.

2. Band structure program: Use a large super cell and cut hopping to localized level on one atom in super cell.

McMahan, Martin, Satpathy, PRB 38, 6650 (88).

Gunnarsson, Andersen, Jepsen, Zaanen, PRB 39, 1708 (89).
Constrained RPA

In RPA the polarizability is written as
\[ P(r, r' : \omega) = \sum_{i}^{\text{occ}} \sum_{j}^{\text{unocc}} \psi_i(r) \psi_i^*(r') \psi_j^*(r) \psi_j(r') \]
\[ \times \left( \frac{1}{\omega - \epsilon_j + \epsilon_i + i0^+} - \frac{1}{\omega + \epsilon_j - \epsilon_i - i0^+} \right) \]

Calculating a screened Coulomb interaction would involve double-counting. Screening of 3d-electrons by 3d electrons both in \( U^{\text{eff}} \) and in Hubbard model.

Remove transitions where both occupied and unoccupied states contain 3d-states by introducing an energy window around 3d-band.

Results sensitive to precise choice of window.


## $U$ for Mn in CdTe

### Mn atom

<table>
<thead>
<tr>
<th>Term</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Unrenormalized ($F^0$)</td>
<td>21.4 eV</td>
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<tr>
<td>Relaxation of $3d$ orbital</td>
<td>-5.2 eV</td>
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<tr>
<td>Relaxation of $4s, 4p$ orbitals</td>
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<tr>
<td>Relaxation core, XC effects</td>
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<tr>
<td><strong>Atomic $U$</strong></td>
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### Mn in CdTe

<table>
<thead>
<tr>
<th>Term</th>
<th>Value</th>
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<tbody>
<tr>
<td>On-site relaxation</td>
<td>15.4 eV</td>
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<tr>
<td>Charge transfer from Mn</td>
<td>-7.6 eV</td>
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<tr>
<td>Charge transfer to n.n. ligand</td>
<td>-0.4 eV</td>
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<tr>
<td><strong>Solid state $U$</strong></td>
<td>7.4 eV</td>
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Screening charge. Mn in CdTe

### Screening charge

<table>
<thead>
<tr>
<th>State</th>
<th>Screening charge</th>
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<tbody>
<tr>
<td>Mn $4s$</td>
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</tr>
<tr>
<td>Mn $4p$</td>
<td>25 %</td>
</tr>
<tr>
<td>Te</td>
<td>25 %</td>
</tr>
<tr>
<td>Empty</td>
<td>19 %</td>
</tr>
</tbody>
</table>

Only about half the screening charge sits on Mn.

Gunnarsson, Andersen, Jepsen, Zaanen, PRB 39, 1708 (89).
“Cut off” method: $U \sim 6.2$ eV. Screening: 4s 24 %, 4p 29 %.

**Simple estimate of screening charge:**

Shift of $4sp$ levels:

$$\Delta E_s = F^0(3d, 4s) - \delta n_{4sp} F^0(4s, 4s) - \frac{2}{d}(1 - \delta n_{4sp})$$

Screening charge $\delta n_{4sp} = N(0) \Delta E_s$.

$F^0(3d, 4s) = 1.01$ Ry, $F^0(4s, 4s) = 0.89$ Ry, $d = 4.68$ $a_0$, $N(0) = 2$ states/Ry. $\Rightarrow \delta n_{4sp} = 0.61$. Calc. 0.53.

**Simple estimate of $U$:**

$$U = \frac{\partial \varepsilon_{3d}}{\partial n_{3d}}$$

$$U \approx F(3d, 3d) - \delta n_{4sp} F(3d, 4s) - (1 - \delta n_{4sp}) \frac{2}{d}$$

$$= F(3d, 3d) - \delta n_{4sp} [F(3d, 4s) - \frac{2}{d}] - \frac{2}{d} \approx 16.2 - 7.9 \delta n_{4sp} - 5.8.$$

“Perfect screening” $\Rightarrow$ $U \sim 2.5$ eV (renormalized atom 2.7 eV).

Anisimov, Gunnarsson, PRB 43, 7570 (1991)
## Results for Fe and Ce

<table>
<thead>
<tr>
<th>System</th>
<th>cLDA</th>
<th>“cut-off”</th>
<th>cRPA</th>
<th>“perfect screening”</th>
<th>Exp</th>
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<td>6.2(^2)</td>
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Charge transfer energy

Cuprates:

Keep Cu $3d$ and O $2p$ levels. Need relative energy of these levels.

Nominally: $\text{Cu}^{2+}(3d^9)\text{O}^{2−}(2p^6)$

Consider the hopping of an O electron into the Cu $3d^9$ shell.

Thus we calculate

$$E(3d^{10}L^{-1}) - E(3d^9) \approx \varepsilon_{3d}(n_{3d} = 9.5) - \varepsilon_{2p}(n_{3d} = 9.5).$$

This can be done if, e.g., the hopping integrals are cut.

But results depend crucially on precise definition of $3d$ orbital.
Photoemission Nd$_2$CuO$_4$ (end of $3d$ series)

Electron-doped high-$T_c$ cuprate.

Multiplet integrals from atomic data.

Satellite due to two-hole bound state. Position dep. on $U$.

$U$ ("cut off"):

Stuttgart group $U=8$ eV.

McMahan, Martin, Satpathy $U=8.5$ eV.

$U$ (cLDA):

Hybertsen, Schlüter, Christensen $U=10.5$ eV.

Agreement with experiment suggests a rather accurate $U$.

Neglected renormalizations

Methods for calculating renormalized parameters non-rigorous.

Involving uncontrolled approximations.

Here two examples:


2. XAS like enhancement of hopping matrix elements.
Configuration dependence of hopping matrix elements

LMTO: Hopping integral proportional to $V^2 \sim \tilde{\Delta} \approx \frac{s}{2} \left[ \phi_l(C, s) \right]^2$

$\phi_l(C, s)$ is wavefunction at WS radius $s$ with logarithmic derivative $-l - 1$.

$\phi_l(C, s)$ sensitive to configuration.

Increase # of val. elec. $n_l \Rightarrow \phi_l(C, r)$ expands $\Rightarrow \phi_l(C, s)$ larger.

Core hole (reduce $n_c$) $\Rightarrow \phi_l(C, r)$ contracts $\Rightarrow \phi_l(C, s)$ smaller.

Consider hopping $4f^n \rightarrow 4f^{n+1} L^{-1}$

Use $\phi_l(C, s)$ for configuration $4f^n$ or $4f^{n+1}$ or some average?

Difference more than factor of two $V^2$!

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Configuration dependence of hopping matrix elements

\[ \tilde{\Delta} \times 100 \text{ [Ry]} \]

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Model with breathing

Introduce orbital at standard configuration \( n_l^0 \)
and derivative with respect to \( n_l \)

\[
\phi_i^0 \equiv \phi_i(r, n_l^0)
\]

\[
\phi_i^1 \equiv A \frac{\partial}{\partial n_l} \phi_i(r, n_l)|_{n_l=n_l^0}
\]

Anderson impurity model with \( \phi_i^0 \) and \( \phi_i^1 \). Describes breathing.

Project out high-lying states \( \Rightarrow \) Model with one orbital, but with
prescription for hopping matrix element.

Mixing of two orbitals

\[
\tilde{U} \sum_{m\sigma} (\psi_{1m\sigma}^\dagger \psi_{0m\sigma} + \text{H.c.})(n_0 + n_1 - n_l^0)
\]

\( n^0 + n^1 = n_l^0 \): No mixing in of \( \phi_i^1 \).
\( n^0 + n^1 \neq n_l^0 \): Mixing in \( \phi_i^1 \).

Mn: \( \tilde{U} = 0.16 \text{ Ry} \). \( \varepsilon_i^1 - \varepsilon_i^0 = 2.13 \text{ Ry} \).
\( \frac{|\tilde{U}|}{(\varepsilon_i^1 - \varepsilon_i^0)} \ll 1 \)

Perturbation theory accurate.
Model with breathing

\[ \varepsilon^1_i - \varepsilon^0_i = 2.13 \text{ Ry is large.} \]

The model tends to have two sets of states separated by \( \varepsilon^1_i - \varepsilon^0_i \).

Project out high-lying states. Then left with low-lying states corresponding to ordinary Anderson model.

Hopping matrix elements:

\[ \langle \tilde{\mu} n_l | H | \tilde{\nu} n_l - 1 \rangle \approx \frac{\phi_l(s,n_l)}{\phi_l(s,n^0_l)} \langle \mu n_l | H | \nu n_l - 1 \rangle |n^0_l\rangle. \]

|\( \nu n_l - 1 \rangle\) config. Anderson model. |\( \tilde{\nu} n_l - 1 \rangle\) renormalized model.

Hopping 4f^0 \rightarrow 4f^1 L^{-1}: Orbital extent for 4f^0 does not matter since orbital empty. Calculate hopping for n^0_l = 1.


Too complicated.
Many-body renormalization of hopping. Anderson model

Discussed: $U_{3d,4s}$ renorm. $U_{3d,3d}$. What about hopping?

Anderson orthogonality catastrophe:

$\langle 0|1 \rangle \rightarrow 0$ as size of system $\rightarrow \infty$.

$|n\rangle$: Ground state of $3d$ space in presence of $n$ $3d$ electrons.

Suggests $V_{3d,4s}^{\text{eff}} = V_{3d,4s} \langle 0|1 \rangle \rightarrow 0$?

Actually closer to X-ray absorption spectroscopy (XAS):

$3d \rightarrow 4s$ makes potential for $4s$ more attractive. Exciton like effect.

Suggests enhanced hopping to low-lying $4s$ states.

XAS spectrum: $S(\omega) \sim (\frac{\omega}{\omega - \omega_0})^\alpha \Theta(\omega - \omega_0)$,

where $\alpha$ depends on phase shifts and is positive. $\omega_0$ threshold.
Many-body renormalization of hopping

No spin degeneracy

\[ H = \sum_{k=1}^{N} \varepsilon_k n_k + \varepsilon_d n_d + \frac{t}{\sqrt{N}} \sum_{k=1}^{N} (\psi_k^{\dagger} \psi_d + \text{H.c.}) + \frac{U_{sd}}{N} \sum_{k=1}^{N} \sum_{l=1}^{N} \psi_k^{\dagger} \psi_l n_d \]

Solve model using ED \((t = 1, 2B = 10)\)

| \(N\) | \(N_{el}\) | \((\bar{1}|\bar{0})\) |
|------|--------|----------------|
| 5    | 3      | .93            |
| 9    | 5      | .89            |
| 13   | 7      | .87            |
| 17   | 9      | .85            |

\[ -\Delta E = \varepsilon_{d}^{\text{calc}} - E(n_d = 1) - E(n_d = 0); U_{sd} = 0. \]

\[ n_d \]

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Renor.: Calculate \(\varepsilon_d^{\text{calc}} = E(n_d = 1) - E(n_d = 0); U_{sd} = 0.\)

Fit: Choose best \(\varepsilon_d^{\text{fit}}\) and \(t_{\text{eff}}^{\text{fit}}; U_{sd} = 0.\)

XAS: \( [t_{\text{eff}}(\varepsilon)]^2 = t^2 S(|\varepsilon - \varepsilon_F + \omega_0|), \varepsilon_d^{\text{calc}}; U_{sd} = 0.\)

XAS and fit comp. \(t_{\text{eff}}^{\text{fit}}\) enhanced. Consistent with Ce comp. results.

Gunnarsson, Schönhammer, PRB 40, 4160 (199).
Many-body renormalization of hopping

\[ -\Delta E \]

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## Many-body renormalization of hopping

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Discovery of Fullerenes

- 60 equivalent carbon atoms.
- 12 Pentagons, 20 Hexagons.
- Same shape as a soccer ball.
- Discovered during astrophysical studies 1985.
- Curl, Kroto, Smalley: Nobel prize 1996.
Narrow band system

Energy scales:

\[ W \sim 0.6 \text{ eV} \quad t_{1u} \text{ one-particle band width} \]
\[ \omega_{ph} \sim 0.2 \text{ eV} \quad \text{Phonon energies} \]
\[ U \sim 1 - 1.5 \text{ eV} \quad \text{On-site Coulomb interaction} \]

Alkali-doped: Gives off electrons to \( t_{1u} \). Often metallic.

Due to unusual parameter range, many interesting issues raised.

1. \( W < U \Rightarrow \text{Correlation important.} \)
2. \( \text{Im } \Sigma_{el-ph} \sim W \Rightarrow \text{Boltzmann equ. questionable } (l << d). \)
3. \( \omega_{ph} \sim W \Rightarrow \text{Retardation effects small. Why large } T_c? \)
4. \( \omega_{ph} \sim W \Rightarrow \text{Migdal’s theorem questionable.} \)

Hopping

$2s$ and $2p \Rightarrow$ approx. $sp^2$ hybrids in $C_{60}$ surface.

Strong coupling. Bonding and anti-bonding states far from $E_F$.

Remaining approx. $p_r$ orbitals couple weakly.

Close to $E_F$. Point towards neighboring mol.

Important for band structure.

Two $2p - 2p$ hopping integrals $V_{pp\sigma}$ and $V_{pp\pi}$:

$$V_{pp\sigma} = v_{\sigma} \frac{R}{R_0} e^{-\lambda(R-R_0)}; \quad \frac{V_{pp\pi}}{V_{pp\sigma}} = -\frac{1}{4} \quad R_0 = 3.1 \text{ Å}.$$ 

Adjust $v_{\sigma}$ to LDA band width and $\lambda$ to lattice parameter dep.
Comparison with LDA band structure

\[ \text{(a)} \]

\[ \text{C}_60 \text{ LDA} \]

\[ \text{(b)} \]

\[ \text{C}_60 \text{ TB} \]

Fm\(\bar{3}\) structure.
Related to \(A_3C_{60}\) structure.

Essential hopping between molecules via to equivalent hopping matrix elements. Determines band width.

Band structure depends primarily on geometrical structure.


Coulomb interaction $U$. $C_{60}$ molecule

Theory:

Simple estimate: Assume the charge of the $(t_{1u})$ orbital is spread out as a thin shell over the $C_{60}$ molecule.

$U_{\text{Molecule}} \sim \frac{e^2}{R} \sim 4 \text{ eV}$. 

This neglects the relaxation of the orbitals as an electron is added to the molecule.

Better: LDA-LMTO

$$U = E(n + 1) + E(n - 1) - 2E(n)$$

$\Rightarrow U \approx 2.7 \text{ eV}$. 

Coulomb interaction $U$. C$_{60}$ molecule

**Experiment:**

\[ U_{\text{Molecule}} = I_p(C^-_{60}) - A(C^-_{60}) \approx 2.7 \text{ eV.} \]

\[ U_{\text{Molecule}} = I_p(C_{60}) - A(C_{60}) - E_g \approx 3.3 \text{ eV.} \]

The two experiment measure different $U$’s!

Experiment 1: Repulsion of two electrons.

Experiment 2: Attraction between electron and hole.

Parameters renormalized differently in diff. experiments!
Coulomb interaction $U$. $C_{60}$ solid

$U$ screened by the polarization of surrounding molecules.

Include dipole interactions between $C_{60}$ molecules self-consistently.

$U_{\text{Solid}} = U_{\text{Molecule}} - \delta U$.

Polarizability $\alpha \sim 90 \, \text{Å}^3 \Rightarrow \delta U \sim 1.7 \, \text{eV}$.

$\Rightarrow U_{\text{Solid}} \sim 2.7 - 1.7 = 1.0 \, \text{eV}$ [Antropov, Gunnarsson, Jepsen, PRB 46, 13647 (1992)].

cRPA: $U \sim 0.8 \, \text{eV}$ [Nomura, Nakamura, Arita, PRB 85, 155452 (2012)].

At surface $U$ screened less efficiently $\Rightarrow U_{\text{Surface}} = 1.3 \, \text{eV}$.

Auger (surface sensitive): $U = 1.4 \, \text{eV}$. 
Estimate of $U$ from Auger spectroscopy

One-particle theory: $T = \varepsilon_{\text{valence}_1} + \varepsilon_{\text{valence}_2} - \varepsilon_{1s}$

Convolute PES spectra.

Two valence holes interact by $U$. Shift convoluted PES spectra by $U$.

Average shift about 1.6 eV. Shift for highest occupied level 1.4 eV.

Phonons and electron-phonon coupling. $A_3C_{60}$

Electron-phonon interaction believed to cause superconductivity. Electron-phonon interaction important for transport properties and electronic properties in general.

1. Librations. $4-5$ meV. $\lambda \sim 0.01$ (Theor.) $\lambda < 0.08$ (Exp.).
2. Intermolecular modes. $0 - 8$ meV. $\lambda \sim 0.01$ (Theory).
3. Alkali modes. $5 - 16$ meV. $\lambda$ “small”.
4. Intramolecular modes. $34-195$ meV. $\lambda \sim 0.5 - 1.0$.

Focus on intramolecular phonons.

$H_g$, $A_g$ intramol. phonons couple to $t_{1u}$ level. $H_g$ Jahn-Teller phonons.
Calculation of electron-phonon coupling

Calculation of electron-phonon coupling for C\textsubscript{60} solids very complicated.

For intramolecular modes: If intramolecular hopping much larger than intermolecular hopping:

\[ \lambda \sim N(0) \sum_{\nu \alpha} \Delta \varepsilon_{\nu \alpha}^2 \frac{\Delta \varepsilon_{\nu \alpha}^2}{\omega_\nu^2}, \]

\( \Delta \varepsilon_{\nu \alpha} \) shift of \( \varepsilon_{\nu \alpha} \) per unit displacement. \( \omega_\nu \) phonon frequency.

MPI-FKF Stuttgart
Results for coupling strength

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\omega_\nu$</th>
<th>$\lambda_\nu / N(0)$</th>
</tr>
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<tr>
<td>$H_g(8)$</td>
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<tr>
<td>$H_g(1)$</td>
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<td>.003 .001 .005 .006</td>
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</table>

$\sum_{H_g} .068 .049 .065 .083$

Antropov, Faulhaber and Manini LDA calculations.

Iwahara hybrid functional B3LYP (20 % HF).

Rather large deviations illustrating numerically difficult calculations.
<table>
<thead>
<tr>
<th>Mode</th>
<th>$\omega_\nu$</th>
<th>Antropov</th>
<th>Faulhaber</th>
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<th>Iwahara</th>
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Sensitivity of coupling to eigenvectors

\[ e_{\nu\tau}^{\text{exact}} = \sum_{\nu'=1}^{8} c_{\nu\nu'} e_{\nu'\tau} \]

\[ \Delta \varepsilon_{\nu\alpha}^{\text{exact}} = \sum_{\nu'=1}^{8} c_{\nu\nu'} \Delta \varepsilon_{\nu'\alpha} \quad \sum_{\nu\alpha} (\Delta \varepsilon_{\nu\alpha}^{\text{exact}})^2 = \sum_{\nu\alpha} (\Delta \varepsilon_{\nu\alpha})^2. \]

\[ \lambda \sim N(0) \sum_{\nu\alpha} \frac{\Delta \varepsilon_{\nu\alpha}^2}{\omega_{\nu}^2}. \]

I. \[ e_{7\tau}^{\text{exact}} = \sqrt{0.95} e_{7\tau} - \sqrt{0.05} e_{8\tau} \]
\[ e_{8\tau}^{\text{exact}} = \sqrt{0.05} e_{7\tau} + \sqrt{0.95} e_{8\tau} \]
\[ \lambda_{7}/N(0) = 0.010, \lambda_{8}/N(0) = 0.030 \text{ instead of} \]
\[ \lambda_{7}/N(0) = 0.020, \lambda_{8}/N(0) = 0.022 \]

II. \[ e_{2\tau}^{\text{exact}} = \sqrt{0.95} e_{2\tau} + \sqrt{0.05} e_{8\tau} \]
\[ e_{8\tau}^{\text{exact}} = \sqrt{0.05} e_{2\tau} - \sqrt{0.95} e_{8\tau} \]
\[ \lambda_{2}/N(0) = 0.033, \lambda_{8}/N(0) = 0.019 \text{ instead of} \]
\[ \lambda_{2}/N(0) = 0.006, \lambda_{8}/N(0) = 0.022 \]

Experimental estimate from Photoemission for free C$_{60}^-$ molecule

As the $t_{1u}$ electron is removed, phonons are excited.

These excitations show up as satellites. Final states very simple.

The weight of satellites give information about electron-phonon coupling.

Photoemission $C_{60}^{-}$

Hamiltonian:

$$H = \varepsilon_0 \sum_{m=1}^{3} \psi_m^\dagger \psi_m + \sum_{\nu=1}^{42} \omega_\nu b_\nu^\dagger b_\nu + \sum_m \sum_n \sum_\nu c_{nm}^\nu \psi_m^\dagger \psi_n (b_\nu + b_\nu^\dagger).$$

1. 3-fold degenerate $t_{1u}$ level.

2. 42 phonon modes; 8 5-fold deg. $H_g + 2 A_g$ modes.


Ground-state: \[ \Phi > = \left[ \sum_{m=1}^{3} a_m \psi_m^\dagger + \sum_{m=1}^{3} \sum_{\nu=1}^{42} a_{m;\nu} \psi_m^\dagger b_\nu^\dagger + \sum_{m;\mu;\nu} a_{m;\mu;\nu} \psi_m^\dagger b_\mu^\dagger b_\nu^\dagger + \ldots \right] |\text{vac}>. \]

Final states: \[ |\text{vac}>; \quad b_\nu^\dagger |\text{vac}>; \quad b_\mu^\dagger b_\nu^\dagger |\text{vac}>. \]

Photoemission spectrum:

$$\rho(\omega) = \sum_s |\langle N - 1, s|c_m|N, 0\rangle|^2 \delta[\omega - E_s (N - 1) + E_0(N)].$$

Solve Hamiltonian and adjust parameters until agreement with exp.
Parameters not unique. Use calculated couplings to $A_g$ phonons.

Total coupling strength $\lambda \sim 1$.

Substantial coupling strength.

But partly canceled by Hund's rule coupling.

Coupling strengths:

<table>
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<tr>
<th>$H_g$ Mode</th>
<th>1</th>
<th>2</th>
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<td>$\lambda_\nu/N(0)$</td>
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Experimental estimate from Raman scattering

Phonon line width $\gamma_\nu$ for mode $\nu$ due to electron-phonon interaction:

$$\gamma_\nu = 2\pi \hbar^2 \omega^2_\nu N(0) \lambda_\nu,$$

where $\omega_\nu$ is the phonon frequency.

Measure change in line width between undoped (insulating) and doped (metallic) fullerides using Raman scattering $\Rightarrow$ estimate of $\lambda_\nu$. 
Theoretical and experimental estimates of $\lambda$

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$$\sum H_g$$ | .068     | .049      | .065   | .083    | .147          | .096  | .083 |

Iwahara photoemission: New high resolution measurement.

Iwahara, Sato, Tanaka, Chibotaru, PRB 82, 245409 (2010).

Reasonable agreement B3LYP, Iwhara photo. Raman total coupling.

Large deviation between Raman and other estimates for coupling strength distribution.

Tendency to move coupling strength to lower modes in solids.
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Spectral weight transfer

Phonon $\nu$ decays in an electron-hole pair.
This pair decays in phonon $\mu$.
Coupling between different phonon modes.

$$H = \sum_{i\nu} \omega_{\nu} b_{i\nu}^\dagger b_{i\nu} + \sum_{i\sigma} \left[ \varepsilon_0 + \sum_{\nu} g_{\nu} (b_{i\nu} + b_{i\nu}^\dagger) \right] n_{i\sigma}$$

$$+ U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \sum_{ij} t_{ij} c_{i\sigma}^\dagger c_{j\sigma}$$

Four sites, two phonon modes.

$$\lambda_1^{\text{eff}} = (1 + c\lambda_2) \lambda_1$$
$$\lambda_2^{\text{eff}} = (1 - c\lambda_2 \left( \frac{\omega_1}{\omega_2} \right)^2) \lambda_2$$

Transfer of spectral weight to lower mode. $U$ reduces phonon width.

Han and Gunnarsson, PRB B 61, 8628 (2000)
Summary

Complicated systems with strong correlation effects: Need for models.

No systematic (practical) procedure for deriving models without uncontrolled assumptions.

Assume two types of electrons, only a few types of Coulomb integrals.

Effects left out included as renormalization of parameters.

Works fairly well for quite a few cases.

But many effects left out.

Parameters property dependent.