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

$$\{-\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + v_{xc}(\mathbf{r})\}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

If good approximation to v_{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

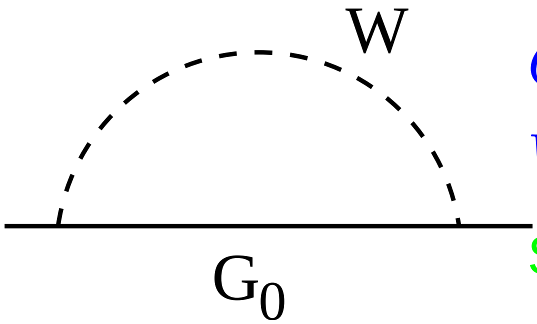
1. No systematic procedure for improving approximations for v_{xc}. For strongly correlated systems, LDA and GGA often not good enough.

2. In principle only ground-state properties. ε_i often (successfully) treated as excitation energies. But even if exact v_{xc} known, ε_i in general *not* an exact excitation energy (But time-dependent DFT).

Need for many-body theory.

GW approximation

Based on diagrammatic theory.

$\Sigma =$ 

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: $YBa_2Cu_3O_7$ (13 atoms); K_3C_{60} (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.

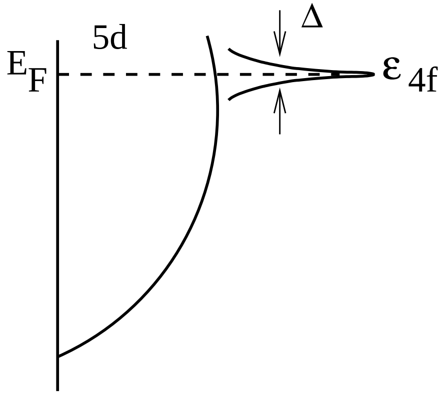
Advantage: Easier to extract physics.

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: α-γ - 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

$$H = \sum_i [-\frac{\hbar^2}{2m} \nabla_i^2 + V_{ext}(\mathbf{r}_i)] + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Find some complete one-particle basis set.

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

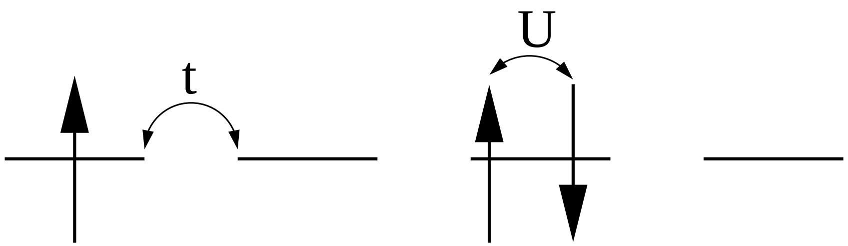
This Hamiltonian can be solved for small atoms and molecules, using, e.g., quantum chemical methods. But it is too complicated for systems we have in mind here.

Need to

1) project out degrees of freedom

2) remove interaction terms

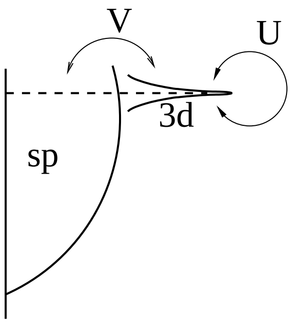
Hubbard model



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

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

Anderson model



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

$$H = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \psi^{\dagger}_{\mathbf{k}\sigma} \psi_{\mathbf{k}\sigma} + \varepsilon_{3d} \sum_{\sigma} \psi^{\dagger}_{\sigma} \psi_{\sigma} + \sum_{\mathbf{k}\sigma} V_{\mathbf{k}} [\psi^{\dagger}_{\mathbf{k}\sigma} \psi_{\sigma} + h.c.] + U n_{\uparrow} n_{\downarrow}.$$

Projecting out one-particle states

$H = \sum_i \varepsilon_i n_i + \sum_{i \neq j} t_{ij} \psi_i^\dagger \psi_j$.

Corresping Hamiltonian matrix:

We study

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

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

Resolvent operator has poles at eigenvalues E_μ.

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

Coulomb integrals: $F_{ij} = e^2 \int d^3r \int d^3r' \frac{\Phi_i^2(\mathbf{r})\Phi_j^2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$.

Mn: $F_{3d,3d} \sim 21$ eV, $F_{3d,4s} \sim 10$ eV,

$F_{nn} \sim 5-6$ eV (nearest neighbor).

Unjustified to keep $F_{3d,3d}$ and neglect everything else. Furthermore $F_{3d,3d} \sim 21$ 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.

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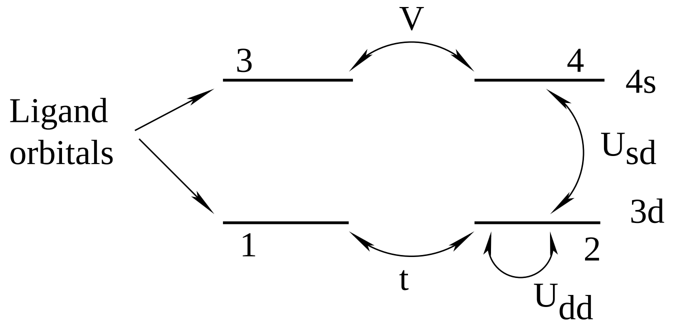
Simple model of 3d impurity

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

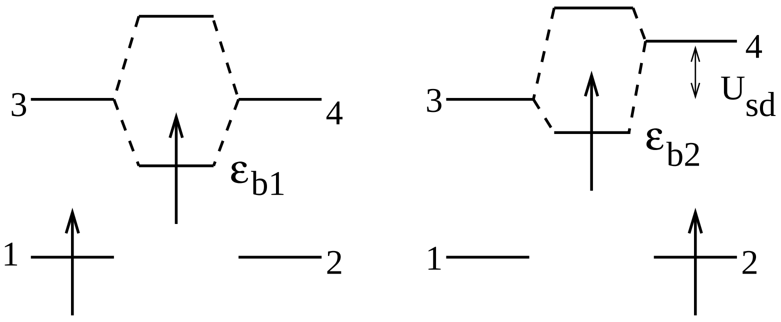
$$+U_{dd} n_{2\uparrow} n_{2\downarrow} + U_{sd}\sum_{\sigma\sigma'} n_{2\sigma}\, n_{4\sigma'}.$$

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



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.



$$\varepsilon_1 = \varepsilon_2 \quad \varepsilon_3 = \varepsilon_4$$
$$\varepsilon_1^{eff} = \varepsilon_1 + \varepsilon_{b1}$$
$$\varepsilon_2^{eff} = \varepsilon_2 + \varepsilon_{b2}.$$

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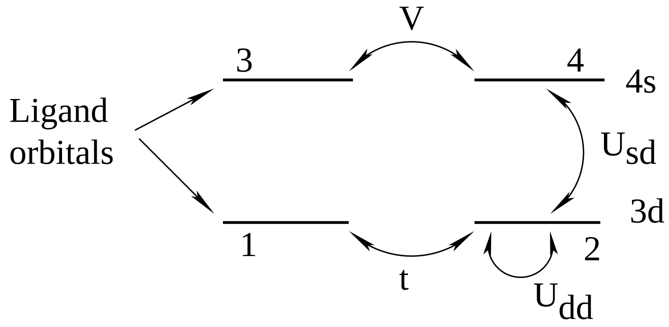
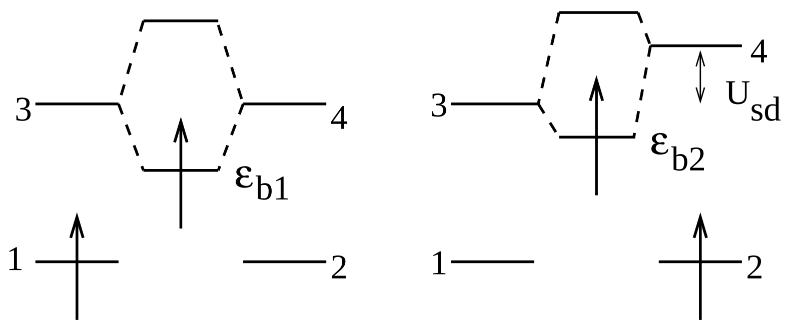




$$\varepsilon_1 = \varepsilon_2 \quad \varepsilon_3 = \varepsilon_4$$

$$\varepsilon_1^{eff} = \varepsilon_1 + \varepsilon_{b1}, \qquad \varepsilon_2^{eff} = \varepsilon_2 + \varepsilon_{b2}.$$

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

$$\varepsilon_2^{eff} - \varepsilon_1^{eff} = \frac{1}{2}U_{sd} - \frac{1}{8}\frac{U_{sd}^2}{V} + O(\frac{1}{V^2}).$$

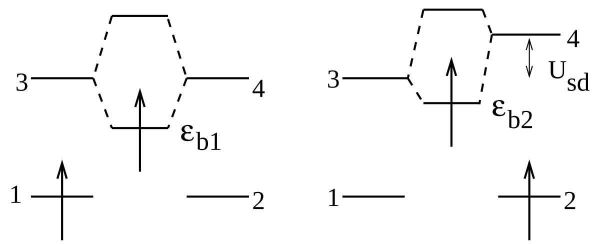
Renormalized by less than $U_{sd}/2$, due to readjustments of charge.

Exact solution

Introduce complete basis set.

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

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



Write down 4×4 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:

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

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

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

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

O. Gunnarsson, PRB **41**, 514 (1990).

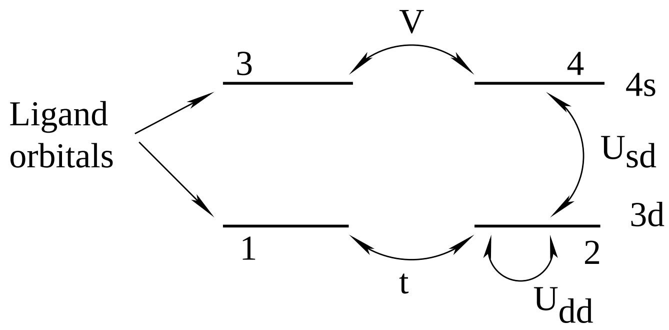
Spin degenerate model.

$$H^{eff}=\sum_\sigma[\varepsilon_1^{eff}n_{1\sigma}+\varepsilon_2^{eff}n_{2\sigma}+t(\psi^\dagger_{1\sigma}\psi_{2\sigma}+\psi^\dagger_{2\sigma}\psi_{1\sigma})]+U^{eff}n_{1\uparrow}n_{1\downarrow}.$$

$$U^{eff}=E(n_2=2)-E(n_2=0)-2E(n=1).$$

$$\varepsilon_2^{eff}-\varepsilon_1^{eff}=U_{sd}-\frac{1}{4}\frac{U_{sd}^2}{V}+O(\frac{1}{V^2}).$$

$$U^{eff}=U-\frac{1}{2}\frac{U_{sd}^2}{V}+O(\frac{1}{V^2}).$$



V	$\varepsilon_2^{\rm eff}$-$\varepsilon_1^{\rm eff}$	$U^{\rm eff}$	E_0+2V		n_2		χ	
			Renorm.	Exact	Renorm.	Exact	Renorm.	Exact
1.0	1.17	3.18	-1.05	-0.95	0.380	0.364	0.314	0.312
1.5	1.39	3.21	-0.97	-0.90	0.339	0.326	0.266	0.262
2.0	1.53	3.29	-0.92	-0.88	0.317	0.307	0.240	0.237
3.0	1.68	3.44	-0.87	-0.85	0.292	0.287	0.214	0.213
4.0	1.75	3.55	-0.85	-0.84	0.280	0.277	0.202	0.201
6.0	1.83	3.68	-0.83	-0.82	0.268	0.267	0.190	0.190
10.0	1.90	3.80	-0.81	-0.81	0.259	0.258	0.181	0.181
20.0	1.95	3.90	-0.80	-0.80	0.252	0.252	0.174	0.174

$t=1$

$U_{dd}=4$

$U_{sd}=2$

Accurate for V large. Two types of electrons.

O. Gunnarsson, PRB **41**, 514 (1990).

Spin degenerate model.

V	$\varepsilon_2^{\rm eff}$-$\varepsilon_1^{\rm eff}$	$U^{\rm eff}$	E_0+2V		n_2		χ	
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O. Gunnarsson, PRB **41**, 514 (1990).

Two types of electrons?

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

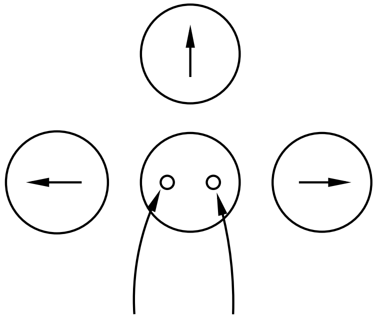
Can we separate electrons of real systems into localized and delocalized?

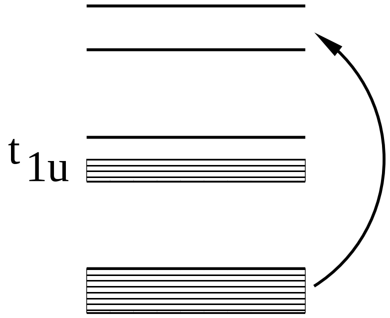
System	Localized	Delocalized
$4f$ compounds	$4f$	$5d$
$3d$ compounds	$3d$	$4s$, $4p$

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= 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.

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“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.

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

$$U = E(5d^2 4f^{n+1}) + E(5d^4 4f^{n-1}) - 2E(5d^3 4f^n).$$

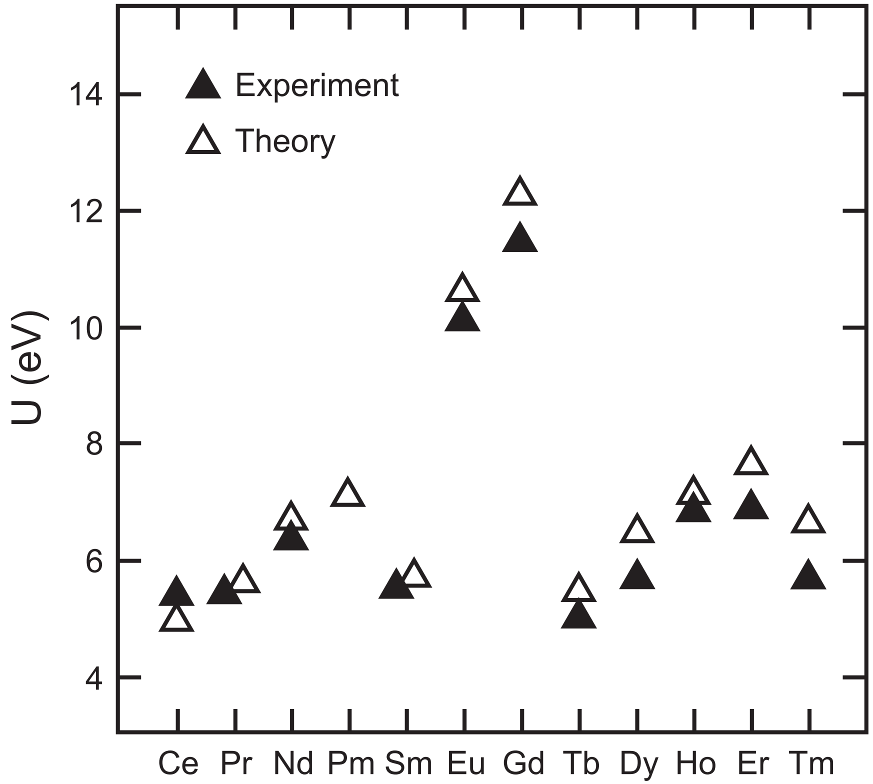
E.g., Ce: $U = E(5d^2 4f^2) + E(5d^4 4f^0) - 2E(5d^3 4f^1)$.

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).

U for rare earths



"Perfect" screening assumed.

"Renormalized" atom calculation

(inside Wigner-Seitz sphere).

Theory: Herbst, Wilkins, Watson, PRB **13**, 1439 (1976); **17**, 3089 (1978).

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.

$$E[n_{3d}^i] = F[n] + \int d^3r V_{ext}(\mathbf{r}) n(\mathbf{r}) + \mu\{\int d^3r n(\mathbf{r}) - N\}$$

$$+\mu_{3d}^i\{\int d^3r n_{3d}^i(\mathbf{r}) - n_{3d}^i\}.$$

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

$$0 = \frac{\partial F}{\partial n} + V_{ext}(\mathbf{r}) + \mu + \mu_{3d}^i P_{3d}^i$$

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

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

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

Dederichs,Blügel, Zeller, Akai, PRL **53**, 2512 (1984).

“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

$$H = \sum_{ij\sigma} t_{ij}\psi^\dagger_{i\sigma}\psi^{i\ \sigma} + \frac{1}{2}\sum\nolimits'_{ij\sigma\sigma'} U_{ij} n_{i\sigma} n_{j\sigma'}$$

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

$$P(\mathbf{r}, \mathbf{r}^{'} : \omega) = \sum_i^{\mathrm{occ}} \sum_j^{\mathrm{unocc}} \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}^{'}) \psi_j^*(\mathbf{r}) \psi_j(\mathbf{r}^{'})$$

$$\times \left(\frac{1}{\omega - \varepsilon_j + \varepsilon_i + i0^+} - \frac{1}{\omega + \varepsilon_j - \varepsilon_i - i0^+} \right)$$

Calculating a screened Coulomb interaction would involve double-counting. Screening of $3d$-electrons by $3d$ electrons both in U^{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.

Aryasetiawan, Karlsson, Jepsen, Schönberger, PRB **74**, 125106 (2006).

Aryasetiawan, Imada, Georges, Kotliar Biermann and Lichtenstein, PRB **70**, 195104 (2004)

U for Mn in CdTe

Mn atom

Unrenormalized (F^0)	21.4 eV
Relaxation of $3d$ orbital	-5.2 eV
Relaxation of $4s$, $4p$ orbitals	-2.2 eV
Relaxation core, XC effects	-1.2 eV
Atomic U	12.8 eV

Relaxation of $3d$ orbital important.

Mn in CdTe

On-site relaxation	15.4 eV
Charge transfer from Mn	-7.6 eV
Charge transfer to n.n. ligand	-0.4 eV
Solid state U	7.4 eV

Charge transfer to $4sp$ important.

Screening charge. Mn in CdTe

Screening charge

State	Screening charge
Mn $4s$	24 $\%$
Mn $4p$	25 $\%$
Te	25 $\%$
Empty	19 $\%$

Only about half the screening charge sits on Mn.

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

Metallic Fe

"Cut off" method: $U \sim 6.2$ eV. Screening: 4s 24 $\%$, 4p 29 $\%$.

Simple estimate of screening charge:

Shift of $4sp$ levels:

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

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:

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

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

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

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

Anisimov, Gunnarsson, PRB **43**, 7570 (1991)

Results for Fe and Ce

System	cLDA	"cut-off"	cRPA	"perfect screening"	Exp
Fe	2.2[1]	6.2[2]	4[3]	2.7[4]	2
Ce	4.5[1]	6[2]	3.2-3.3[3]	5[5]	5-7

1. Cococcioni, Giroconcoli, PRB **71**, 035105 (2005)

2. Anisimov, Gunnarsson, PRB **43**, 7570 (1991)

3. Aryasetiawan, Karlsson, Jepsen, Schönberger, PRB **74**, 125106 (2006).

4. Cox, Coultard, Loyd, J. Phys. F: Metal Physics **4**, 807 (1974)

5. Herbst, Watson, Wilkins, PRB **13**, 1439 (1976)

Charge transfer energy

Cuprates:

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

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

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

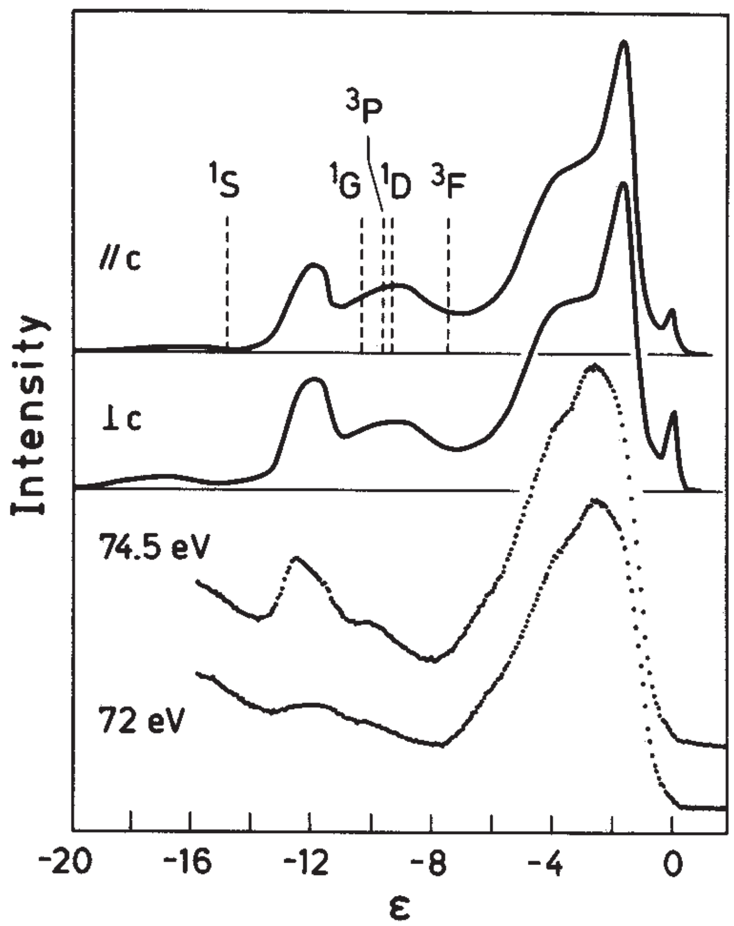
Thus we calculate

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

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

But results depend crucially on precise definition of $3d$ orbital.

Photoemission Nd_2CuO_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.

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Agreement with experiment suggests a rather accurate U.

Gunnarsson, Allen, Jepsen, Fujiwara, Andersen, ..., PRB **41**, 4811 (1990).

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Neglected renormalizations

Methods for calculating renormalized parameters non-rigorous.

Involving uncontrolled approximations.

Here two examples:

1. Configuration dependence of hopping matrix elements.

2. XAS like enhancement of hopping matrix elements.

Configuration dependence of hopping matrix elements

LMTO: Hopping integral proportional to

$V^2 \sim \tilde{\Delta} \approx \frac{s}{2}[\phi_l(C,s)]^2$

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

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

$\tilde{\Delta} \times 100$ [Ry].

n_l	n_c	Mn	Ce	U
$n_l^0 - 1$	n_c^0	.51	0.08	0.72
n_l^0	n_c^0	.85	0.19	0.91
$n_l^0 + 1$	n_c^0	1.29	0.38	1.12
n_l^0	$n_c^0 - 1$	.40	0.05	0.53
$n_l^0 + 1$	$n_c^0 - 1$	.67	0.11	0.69

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!

Configuration dependence of hopping matrix elements

$\tilde{\Delta} \times$ 100 [Ry].

n_l	n_c	Mn	Ce	U
$n_l^0 - 1$	n_c^0	.51	0.08	0.72
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n_l^0	$n_c^0 - 1$	.40	0.05	0.53
$n_l^0 + 1$	$n_c^0 - 1$	.67	0.11	0.69

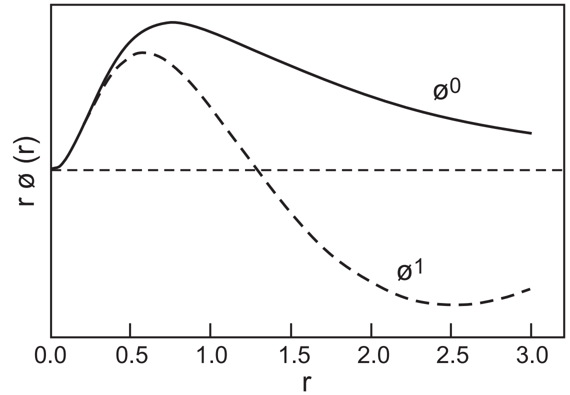
Model with breathing

Introduce orbital at standard configuration n_l^0

and derivative with respect to n_l

$\phi_l^0 \equiv \phi_l(r, n_l^0)$

$\phi_l^1 \equiv A\frac{\partial}{\partial n_l}\phi_l(r, n_l)|_{n_l=n_l^0}$



Anderson impurity model with ϕ_l^0 and ϕ_l^1. Describes breathing.

Project out high-lying states $\Rightarrow$ Model with one orbital, but with

prescription for hopping matrix element.

Mixing of two orbitals

$\tilde{U}\sum_{m\sigma}(\psi^\dagger_{1m\sigma}\psi_{0m\sigma} + \mathrm{H.c.})(n_0 + n_1 - n_l^0)$

$n^0 + n^1 = n_l^0$: No mixing in of ϕ_l^1. $n^0 + n^1 \neq n_l^0$: Mixing in ϕ_l^1.

Mn: $\tilde{U} = 0.16$ Ry. $\varepsilon_l^1 - \varepsilon_l^0 = 2.13$ Ry. $|\tilde{U}|/(\varepsilon_l^1 - \varepsilon_l^0) \ll 1$

Perturbation theory accurate.

Model with breathing

$\varepsilon_l^1 - \varepsilon_l^0 = 2.13$ Ry is large.

The model tends to have two sets of states separated by $\varepsilon_l^1 - \varepsilon_l^0$.

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

Hopping matrix elements:

$\langle \tilde{\mu} n_l | H | \tilde{\nu} n_l - 1 \rangle \approx \frac{\phi_l(s, n_l)}{\phi_l(s, n_l^0)} \langle \mu n_l | H | \nu n_l - 1 \rangle_{n_l^0}$.

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

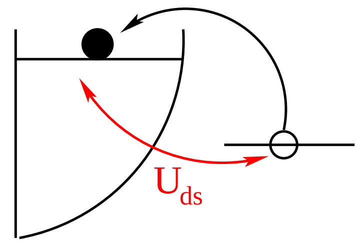
Hopping $4f^0 \to 4f^1 L^{-1}$: Orbital extent for $4f^0$ does not matter since orbital empty. Calculate hopping for $n_l^0 = 1$.

Shows problems. Config. dependent hopping. Property dependent.

Too complicated.

Many-body renormalization of hopping. Anderson model

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



Anderson orthogonality catastrophe:

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

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

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

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

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

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

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

where α depends on phase shifts and is positive. ω_0 threshold.

Many-body renormalization of hopping

No spin degeneracy

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

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

N	N_{el}	$\langle\tilde{1}\vert\tilde{0}\rangle$
5	3	.93
9	5	.89
13	7	.87
17	9	.85

		$-\Delta E$					n_d							
ε_d	U_{sd}	Exact	Renor.	Unre.	Fit	XAS	Exact	Renor.	Unre.	Fit	XAS	$\varepsilon_d^{\rm calc}$	$\varepsilon_d^{\rm fit}$	$t_{\rm eff}^{\rm fit}$
-1.5	1	1.33	1.28	1.66	1.33	1.31	0.89	0.91	0.94	0.89	0.89	-1.09	-1.09	1.12
-1.5	3	0.98	0.83	1.66	0.99	0.94	0.76	0.81	0.94	0.78	0.74	-0.57	-0.64	1.21
-1.5	5	0.83	0.62	1.66	0.88	0.78	0.66	0.70	0.94	0.69	0.62	-0.29	-0.41	1.30
-1.0	3	0.64	0.48	1.20	0.69	0.62	0.57	0.55	0.90	0.55	0.53	-0.07	-0.09	1.31
-0.5	3	0.42	0.29	0.78	0.44	0.41	0.33	0.24	0.79	0.31	0.31	0.43	0.36	1.22
0.0	3	0.29	0.21	0.44	0.30	0.29	0.18	0.11	0.50	0.17	0.17	0.93	0.76	1.15
10	3	.043	.040	.043	.044	.043	.004	.003	.004	.004	.004	10.9	10.1	1.00

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

Fit: Choose best $\varepsilon_d^{\rm fit}$ and $t_{\rm eff}^{\rm fit}$; $U_{sd}=0$.

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

XAS and fit comp. $t_{\rm eff}^{\rm fit}$ enhanced. Consistent with Ce comp. results.

Gunnarsson, Schönhammer, PRB **40**,4160 (199).

Many-body renormalization of hopping

		$-\Delta E$							
ε_d	U_{sd}	Exact	Renor.	Unre.	Fit	XAS	$\varepsilon_d^{\mathrm{calc}}$	$\varepsilon_d^{\mathrm{fit}}$	$t_{\mathrm{eff}}^{\mathrm{fit}}$
-1.5	1	1.33	1.28	1.66	1.33	1.31	-1.09	-1.09	1.12
-1.5	2	1.12	1.02	1.66	1.12	1.08	-0.79	-0.81	1.18
-1.5	3	0.98	0.83	1.66	0.99	0.94	-0.57	-0.64	1.21
-1.5	5	0.83	0.62	1.66	0.88	0.78	-0.29	-0.41	1.30
-1.0	3	0.64	0.48	1.20	0.69	0.62	-0.07	-0.09	1.31
-0.5	3	0.42	0.29	0.78	0.44	0.41	.43	0.36	1.22
0.0	3	0.29	0.21	0.44	0.30	0.29	.93	0.76	1.15
10	3	.043	.040	.043	.044	.043	10.9	10.1	1.00

Many-body renormalization of hopping

		n_d							
ε_d	U_{sd}	Exact	Renor.	Unre.	Fit	XAS	$\varepsilon_d^{\mathrm{calc}}$	$\varepsilon_d^{\mathrm{fit}}$	$t_{\mathrm{eff}}^{\mathrm{fit}}$
-1.5	1	0.89	0.91	0.94	0.89	0.89	-1.09	-1.09	1.12
-1.5	2	0.82	0.87	0.94	0.83	0.81	-0.79	-0.81	1.18
-1.5	3	0.76	0.81	0.94	0.78	0.74	-0.57	-0.64	1.21
-1.5	5	0.66	0.70	0.94	0.69	0.62	-0.29	-0.41	1.30
-1.0	3	0.57	0.55	0.90	0.55	0.53	-0.07	-0.09	1.31
-0.5	3	0.33	0.24	0.79	0.31	0.31	0.43	0.36	1.22
0.0	3	0.18	0.11	0.50	0.17	0.17	0.93	0.76	1.15
10	3	.004	.003	.004	.004	.004	10.9	10.1	1.00

Many-body renormalization of hopping

				χ_c					
ε_d	U_{sd}	Exact	Renor.	Unre.	Fit	XAS	$\varepsilon_d^{\mathrm{calc}}$	$\varepsilon_d^{\mathrm{fit}}$	$t_{\mathrm{eff}}^{\mathrm{fit}}$
-1.5	1	0.12	0.10	0.05	0.12	0.13	-1.09	-1.09	1.12
-1.5	2	0.20	0.19	0.05	0.20	0.23	-0.79	-0.81	1.18
-1.5	3	0.27	0.30	0.05	0.28	0.32	-0.57	-0.64	1.21
-1.5	5	0.36	0.55	0.05	0.38	0.40	-0.29	-0.41	1.30
-1.0	3	0.47	0.74	0.12	0.50	0.47	-0.07	-0.09	1.31
-0.5	3	0.41	0.41	0.35	0.43	0.37	0.43	0.36	1.22
0.0	3	0.21	0.14	0.75	0.22	0.19	0.93	0.76	1.15
10	3	.0006	.0005	.0006	.0006	.0006	10.9	10.1	1.00

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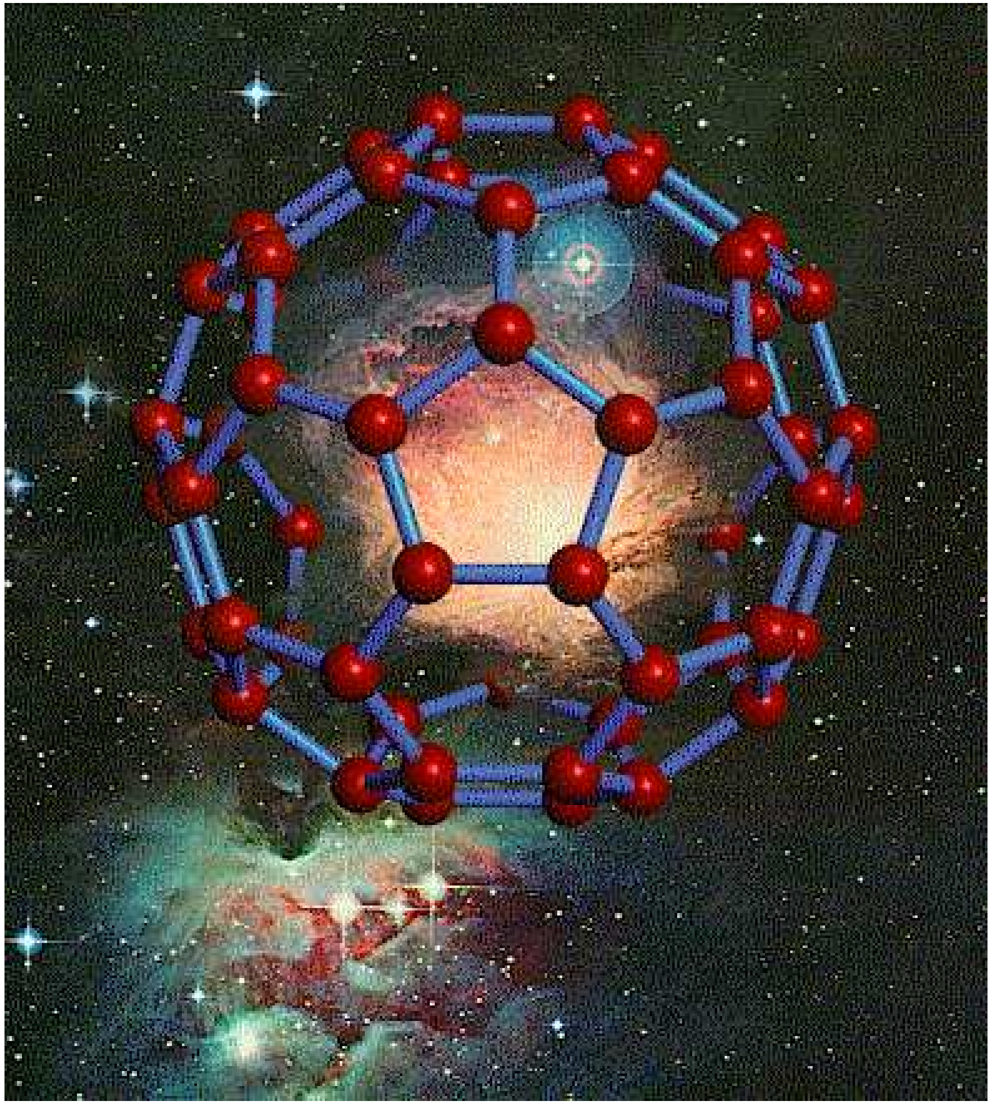
Discovery of Fullerenes



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

Narrow band system

Energy scales:

$W \sim 0.6$ eV — t_{1u} one-particle band width

$\omega_{ph} \sim 0.2$ eV — Phonon energies

$U \sim 1 - 1.5$ eV — On-site Coulomb interaction

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

Due to unusual parameter range, many interesting issues raised.

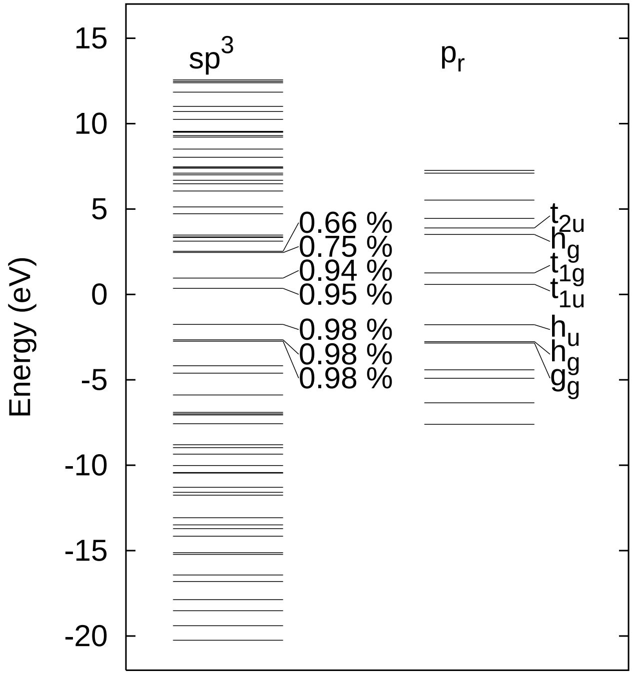
1. $W < U \Rightarrow$ Correlation important.
2. Im $\Sigma_{el-ph} \sim W \Rightarrow$ Boltzmann equ. questionable ($l << d$).
3. $\omega_{ph} \sim W \Rightarrow$ Retardation effects small. Why large T_c?
4. $\omega_{ph} \sim W \Rightarrow$ Migdal's theorem questionable.

Organics: Cano-Cortes, Dolfen, Merino, Behler, Delley, Reuter, and Koch, Eur. Phys. J. B **56**, 173 (2007).

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.

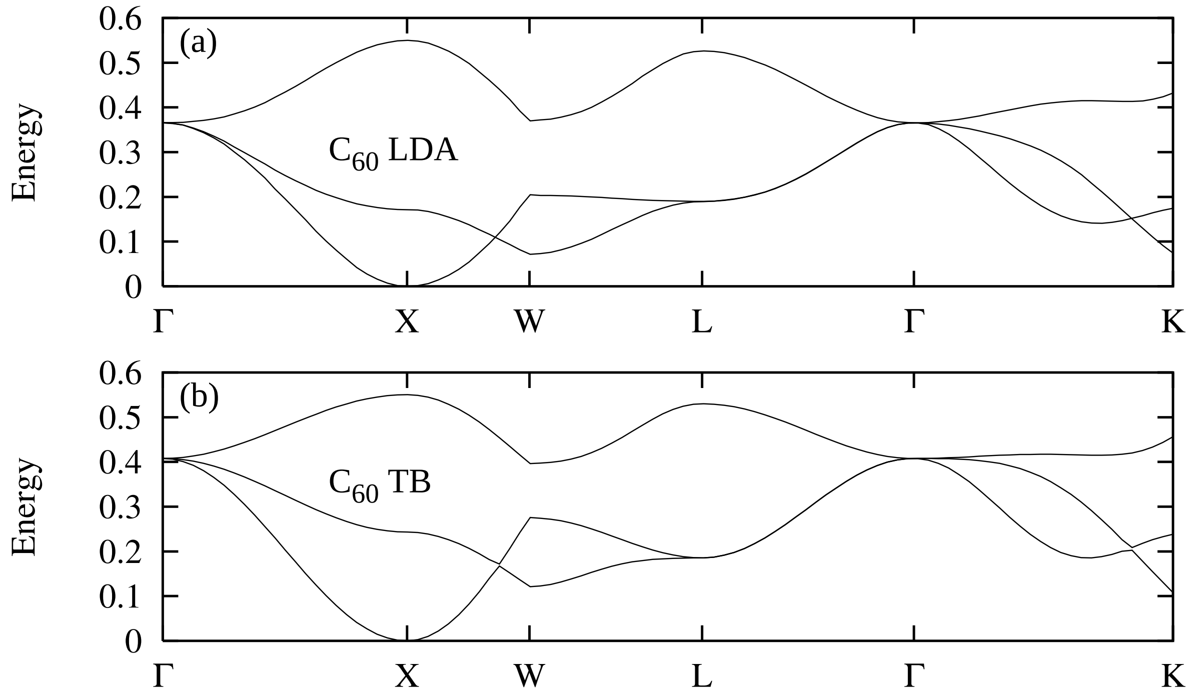


Two $2p - 2p$ hopping integrals $V_{pp\sigma}$ and $V_{pp\pi}$:

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

Adjust v_σ to LDA band width and λ to lattice parameter dep.

Comparison with LDA band structure



$Fm\bar{3}$ 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.

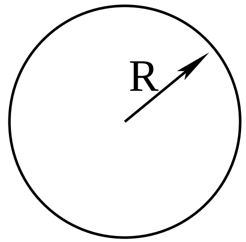
Gunnarsson, Erwin, Koch, and Martin, PRB **57**, 2159 (1998).

Satpathy, Antropov, Andersen, Jepsen, Gunnarsson, and Liechtenstein, PRB **46**, 1773 (1992).

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.



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

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

Better: LDA-LMTO $\quad U = E(n+1) + E(n-1) - 2E(n)$

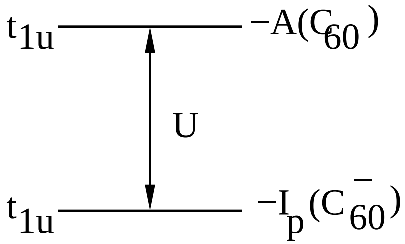
$\Rightarrow U \approx 2.7$ eV.

Antropov, Gunnarsson, Jepsen, PRB **46**, 13647 (1992).

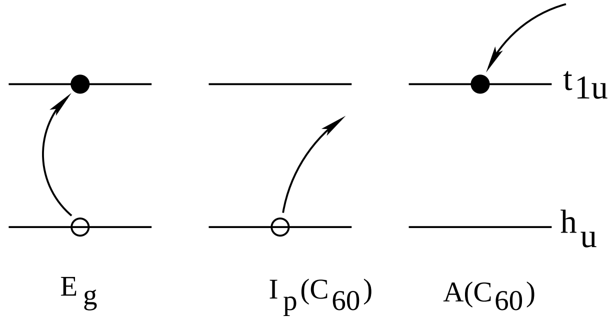
Coulomb interaction U. C_{60} molecule

Experiment:

$$U_{\rm Molecule}=I_p(C_{60}^-)-A(C_{60}^-)\approx 2.7 \text{ eV.}$$



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



The two experiment measure different U's!

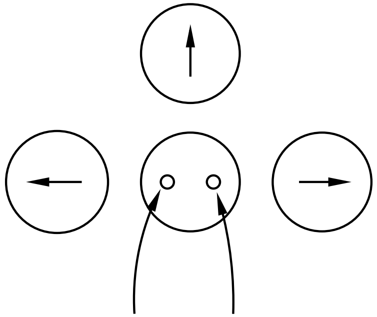
Experiment 1: Repulsion of two electrons.

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.

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

Polarizability $\alpha \sim 90$ Å$^3 \Rightarrow \delta U \sim 1.7$ eV.

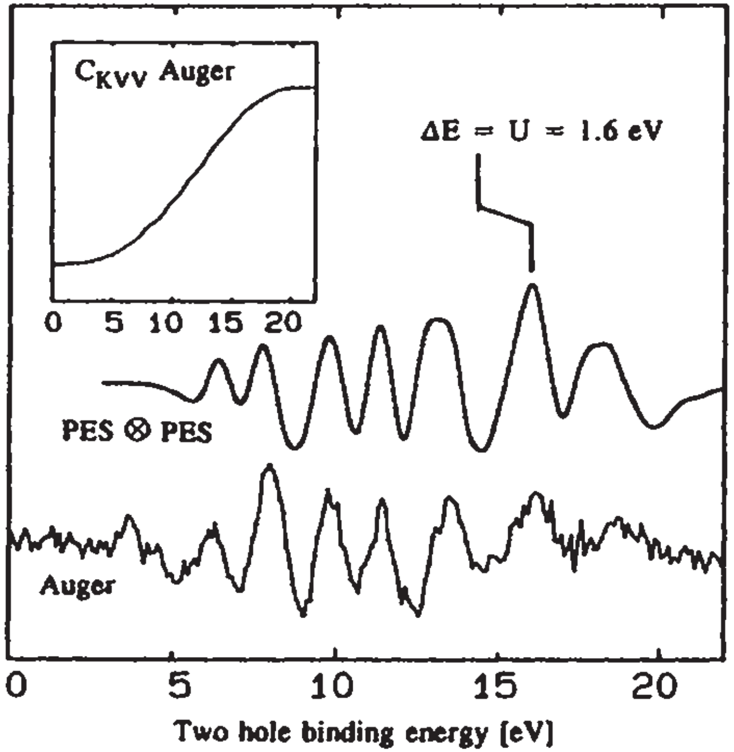
$\Rightarrow U_{\rm Solid} \sim 2.7 - 1.7 = 1.0$ eV [Antropov, Gunnarsson, Jepsen, PRB **46**, 13647 (1992)].

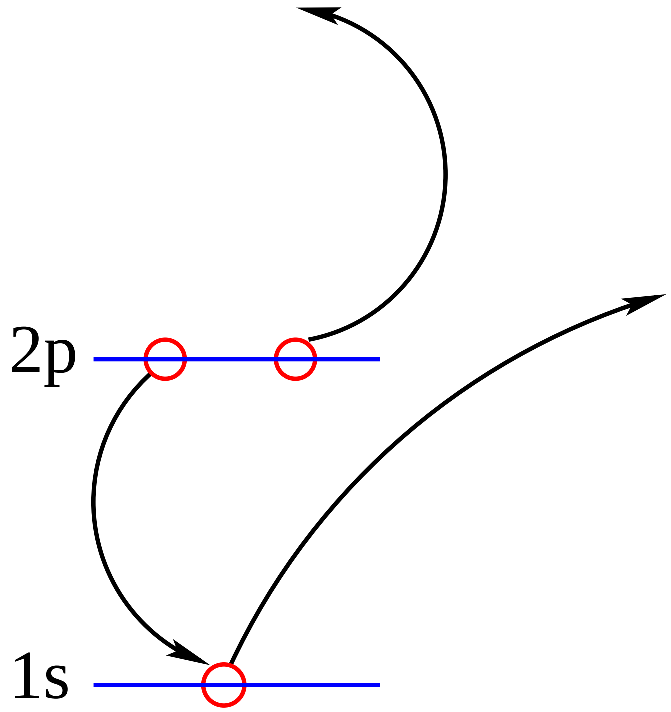
cRPA: $U \sim 0.8$ eV [Nomura, Nakamura, Arita, PRB **85**, 155452 (2012)].

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

Auger (surface sensitive): $U = 1.4$ eV.

Estimate of U from Auger spectroscopy





One-particle theory: $T = \varepsilon_{\text{valence1}} + \varepsilon_{\text{valence2}} - \varepsilon_{1s}$

Convolute PES spectra.

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

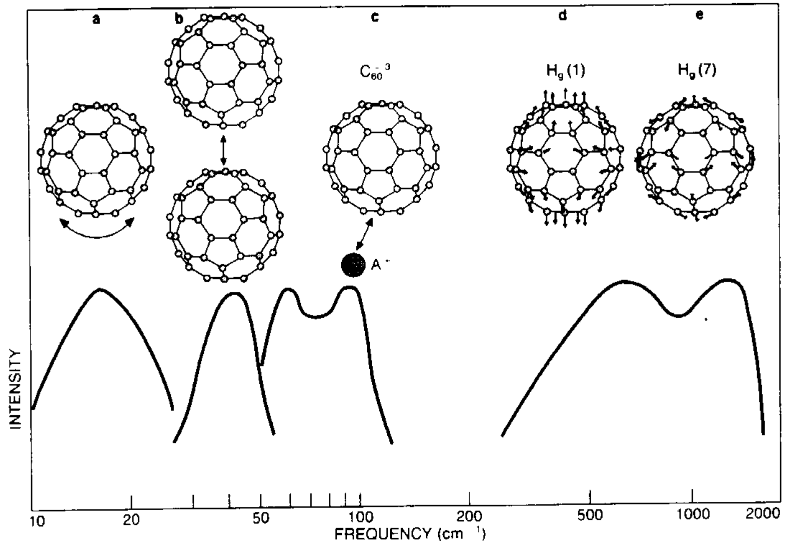
Average shift about 1.6 eV. Shift for highest occupied level 1.4 eV.

Lof, van Veenendaal, Koopmans, Jonkman, and Sawatzky, PRL **68**, 3924 (1992).

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. λ "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$_{60}$ solids very complicated.

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

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

$\Delta\varepsilon_{\nu\alpha}$ shift of $\varepsilon_{\nu\alpha}$ per unit displacement. ω_ν phonon frequency.

Results for coupling strength

		$\lambda_\nu/N(0)$			
Mode	ω_ν	Antropov	Faulhaber	Manini	Iwahara
$H_g(8)$	1575	.022	.009	.014	.018
$H_g(7)$	1428	.020	.015	.015	.023
$H_g(6)$	1250	.008	.002	.003	.002
$H_g(5)$	1099	.003	.002	.004	.005
$H_g(4)$	774	.003	.010	.004	.006
$H_g(3)$	710	.003	.001	.009	.012
$H_g(2)$	437	.006	.010	.011	.011
$H_g(1)$	273	.003	.001	.005	.006
$\sum H_g$		.068	.049	.065	.083

Antropov, Gunnarsson, and Liechtenstein, PRB **48**, 7651 (1993).
Faulhaber, Ko, and Briddon, PRB **48**, 661 (1993).
Manini, Corso, Fabrizio, and Tosatti, Phil. Mag. B **81**, 793 (2001).
Iwahara, Sato, Tanaka, Chibotaru, PRB **82**, 245409 (2010).

Antropov, Faulhaber and Manini LDA calculations.

Iwahara hybrid functional B3LYP (20 $\%$ HF).

Rather large deviations illustrating numerically difficult calculations.

		$\lambda_\nu/N(0)$			
Mode	ω_ν	Antropov	Faulhaber	Manini	Iwahara
H$_g$(8)	1575	.022	.009	.014	.018
H$_g$(7)	1428	.020	.015	.015	.023
H$_g$(6)	1250	.008	.002	.003	.002
H$_g$(5)	1099	.003	.002	.004	.005
H$_g$(4)	774	.003	.010	.004	.006
H$_g$(3)	710	.003	.001	.009	.012
H$_g$(2)	437	.006	.010	.011	.011
H$_g$(1)	273	.003	.001	.005	.006
$\sum$ H$_g$		.068	.049	.065	.083

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Sensitivity of coupling to eigenvectors

$$e^{\mathrm{exact}}_{\nu\tau} = \sum_{\nu'=1}^{8} c_{\nu\nu'} e_{\nu'\tau}$$

$$\Delta\varepsilon^{\mathrm{exact}}_{\nu\alpha} = \sum_{\nu'=1}^{8} c_{\nu\nu'} \Delta\varepsilon_{\nu'\alpha} \quad \sum_{\nu\alpha} (\Delta\varepsilon^{\mathrm{exact}}_{\nu\alpha})^2 = \sum_{\nu\alpha} (\Delta\varepsilon_{\nu\alpha})^2.$$

$$\lambda \sim N(0) \sum_{\nu\alpha} \frac{\Delta\varepsilon^2_{\nu\alpha}}{\omega^2_\nu}.$$

I. $e^{\mathrm{exact}}_{7\tau} = \sqrt{0.95} e_{7\tau} - \sqrt{0.05} e_{8\tau}$

$e^{\mathrm{exact}}_{8\tau} = \sqrt{0.05} e_{7\tau} + \sqrt{0.95} e_{8\tau}$

$\lambda_7/N(0) = 0.010$, $\lambda_8/N(0) = 0.030$ instead of

$\lambda_7/N(0) = 0.020$, $\lambda_8/N(0) = 0.022$

II. $e^{\mathrm{exact}}_{2\tau} = \sqrt{0.95} e_{2\tau} + \sqrt{0.05} e_{8\tau}$

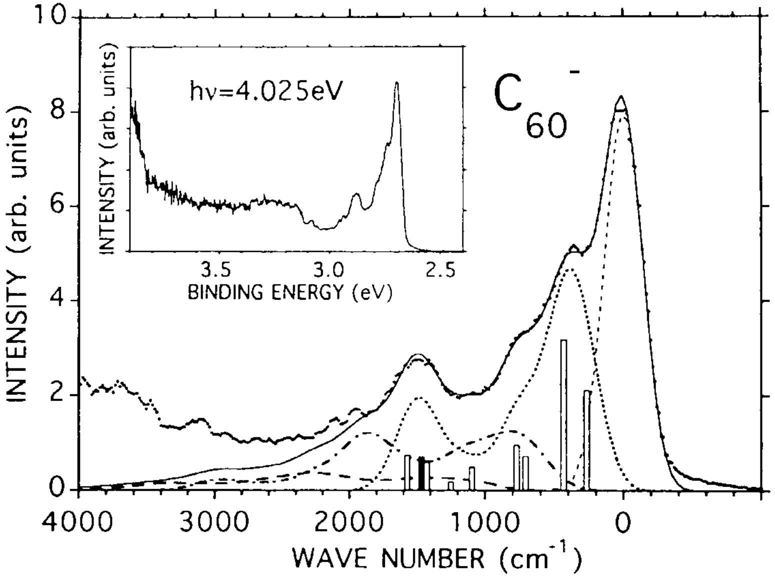
$e^{\mathrm{exact}}_{8\tau} = \sqrt{0.05} e_{2\tau} - \sqrt{0.95} e_{8\tau}$

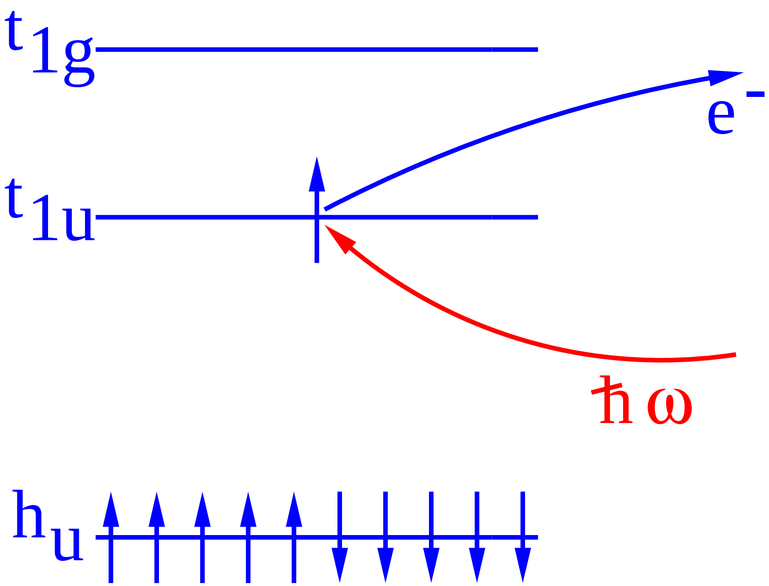
$\lambda_2/N(0) = 0.033$, $\lambda_8/N(0) = 0.019$ instead of

$\lambda_2/N(0) = 0.006$, $\lambda_8/N(0) = 0.022$

Antropov, Gunnarsson, Liechtenstein, PRB **48**, 7651 (1993).

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.

Gunnarsson, Handshuh, Bechthold, Kessler, Ganteför, and Eberhardt, PRL **74**, 1875 (1995).

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.

3. Electron-phonon interaction.

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

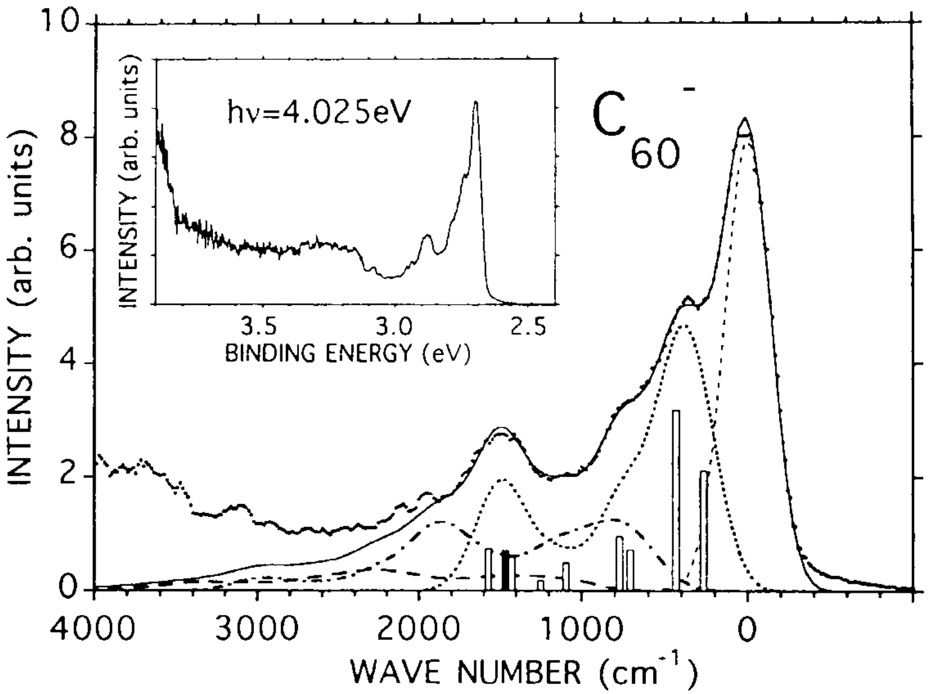
Final states: $|vac>$; $\quad b_\nu^\dagger|vac>$; $\quad b_\mu^\dagger b_\nu^\dagger|vac>$.

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.

Photoemission C_{60}^-



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:

H_g Mode	1	2	3	4	5	6	7	8
$\lambda_\nu/N(0)$	.019	.040	.013	.018	.012	.005	.017	.023

Gunnarsson, Handshuh, Bechthold, Kessler, Ganteför, and Eberhardt, PRL **74**, 1875 (1995).

Experimental estimate from Raman scattering

Phonon line width γ_ν for mode ν due to electron-phonon interaction:

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

where ω_ν is the phonon frequency.

Measure change in line width between undoped (insulating) and doped (metallic) fullerides using Raman scattering $\Rightarrow$ estimate of λ_ν.

Theoretical and experimental estimates of λ

	Theory				Photoemission		Raman
ω_ν	Antropov	Faulhaber	Manini	Iwahara	Gunnarsson	Iwahara	Kuzmany
1575	.022	.009	.014	.018	.023	.011	.003
1428	.020	.015	.015	.023	.017	.028	.004
1250	.008	.002	.003	.002	.005	.007	.001
1099	.003	.002	.004	.005	.012	.009	.001
774	.003	.010	.004	.006	.018	.007	.003
710	.003	.001	.009	.012	.013	.015	.003
437	.006	.010	.011	.011	.040	.012	.020
273	.003	.001	.005	.006	.019	.007	.048
$\sum$ 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.

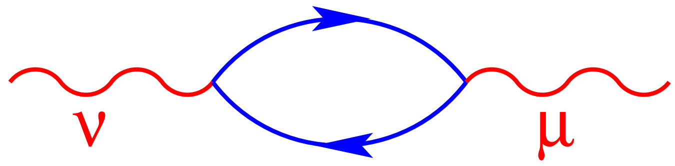
	Theory				Photoemission		Raman
ω_ν	Antr.	Faulh.	Manini	Iwah.	Gunnar.	Iwah.	Kuzmany
1575	.022	.009	.014	.018	.023	.011	.003
1428	.020	.015	.015	.023	.017	.028	.004
1250	.008	.002	.003	.002	.005	.007	.001
1099	.003	.002	.004	.005	.012	.009	.001
774	.003	.010	.004	.006	.018	.007	.003
710	.003	.001	.009	.012	.013	.015	.003
437	.006	.010	.011	.011	.040	.012	.020
273	.003	.001	.005	.006	.019	.007	.048
$\sum$ H$_g$	.068	.049	.065	.083	.147	.096	.083

Spectral weight transfer

Phonon ν decays in an electron-hole pair.

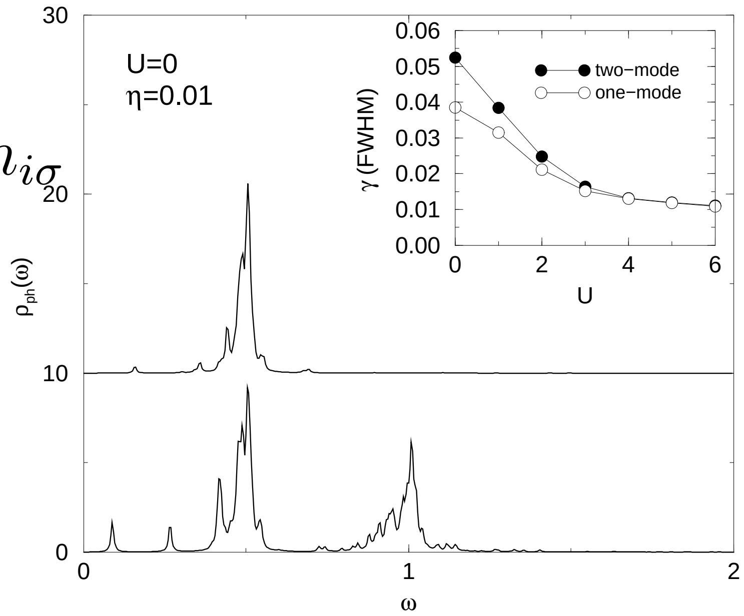
This pair decays in phonon μ.

Coupling between different phonon modes.



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

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



Four sites, two phonon modes.

$\lambda_1^{\rm eff}$=$(1 + c\lambda_2)\lambda_1$ $\quad W$=3.7, ω_1=0.5, ω_2=1,

$\lambda_2^{\rm eff}$=$(1 - c\lambda_2(\frac{\omega_1}{\omega 2})^2)\lambda_2$ $\quad g_1$=0.3, g_2=0.4

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.

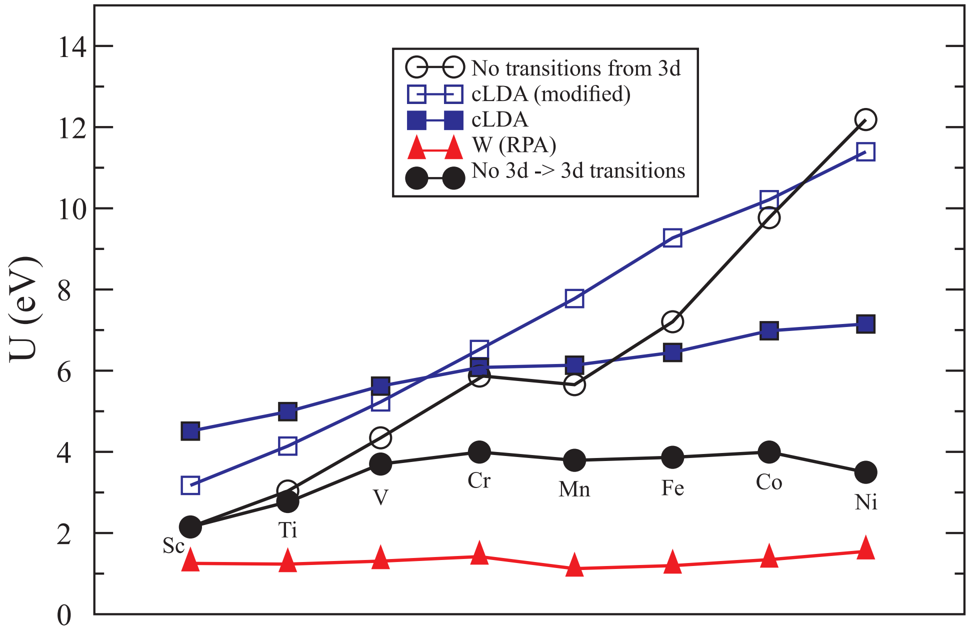
Assume two types of electrons, only a few types of Coulomb integrals.

Effects left out included as renormalization of parameters.

Works fairly well for quite a few cases.

But many effects left out.

Parameters property dependent.



No transitions from 3d
cLDA (modified)
cLDA
W (RPA)
No 3d -> 3d transitions
U (eV)
0
2
4
6
8
10
12
14
Sc
Ti
V
Cr
Mn
Fe
Co
Ni