Models derived from non-convergent perturbation theory and misleading parameter estimates: the case of superexchange

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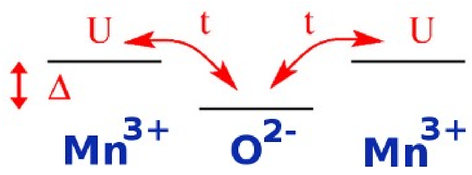
•Studied electron kinetic exchange analytically
• Found that double-scale series expansions are invalid as in multi-variable systems they are not generally convergent
• Fitting a model outside its convergence region to experimental data can lead to misleading conclusions about material parameters (hopping parameters, electron-transfer rates, *etc.*)

Prototypical energy-level model of Anderson



Site-centred Wannier orbitals in MnO and associated energies for the Anderson-Hubbard model. The site energy difference Δ is defined as ε_d-ε_p. U is the Coulomb repulsion and t is the nearest-neighbour hopping.

Anderson-Hubbard model

$$H = \sum_{i,\sigma} \epsilon_i n_{i,\sigma} - t \sum_{\langle i,j\rangle,\sigma} \left(c^\dagger_{i,\sigma} c_{j,\sigma} + c^\dagger_{j,\sigma} c_{i,\sigma} \right) + U \sum_i n_{i,\uparrow} n_{i,\downarrow}$$

Block tri-diagonal form: $H = \left(\begin{array}{c|c|c} H_{00} & T_{01} & 0 \\ \hline T_{10} & H_{11} & T_{12} \\ \hline 0 & T_{21} & H_{22} \end{array}\right)$

Basis of nine antiferromagnetic electron configurations:

$$\begin{aligned} &\text{block 0}: && |\uparrow,\uparrow\downarrow,\downarrow\rangle\,, |\downarrow,\uparrow\downarrow,\uparrow\rangle \\ &\text{block 1}: && |\uparrow\downarrow,\uparrow,\downarrow\rangle\,, |\uparrow\downarrow,\downarrow,\uparrow\rangle\,, |\uparrow,\downarrow,\uparrow\downarrow\rangle\,, |\downarrow,\uparrow,\uparrow\downarrow\rangle \\ &\text{block 2}: && |\uparrow\downarrow,\cdot,\uparrow\downarrow\rangle\,, |\uparrow\downarrow,\uparrow\downarrow,\cdot\rangle\,, |\cdot,\uparrow\downarrow,\uparrow\downarrow\rangle \end{aligned}$$

Exchange is defined as the energy difference between the lowest singlet and triplet configurations. Superexchange is the specific case of kinetic exchange between separated electrons. In this case we are study superexchange between lone spins on the Mn ions.

Solution methods

We employ effective Hamiltonians, derived *exactly*, for the calculation of the superexchange $J=E(T)-E(S)$. The purpose of effective Hamiltonians is to project the full system onto a small subset of the basis (here the H_{00} block).

An exact projection is found using a resolvent approach (other methods such as *e.g.* Brillouin-Wigner perturbation theory are not exact):

$$H_{\text{eff}}(E) = H_{00} + T_{01}\left(E - (H_{11} + T_{12}(E - H_{22})^{-1}T_{21})\right)^{-1} T_{10}$$

The cost of the projection: an energy dependence.
Exact only at the eigenvalue – two different effective Hamiltonians are thus used, for $E(T)$ and $E(S)$ respectively.

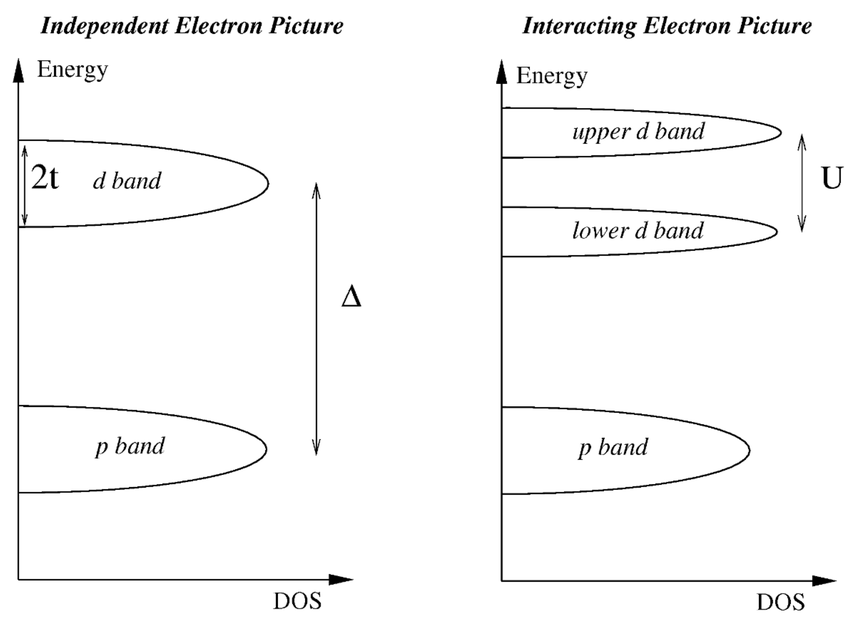
Eigenvalue equation: $H_{\text{eff}}(E)X = EX$ with $X = |\uparrow,\uparrow\downarrow,\downarrow\rangle \pm |\downarrow,\uparrow\downarrow,\uparrow\rangle$

By solving for the roots of $\lambda_i(E)=E$ for $i=S,T$ we find $E(T)$ and $E(S)$.

Series expansions

- multi-variable expressions require careful attention
- single-scale expansion *e.g.* $t \to 0$ or $U \to \infty$
- double-scale expansion *e.g.* $t \ll U$ *- radius of convergence not stable with respect to the expansion procedure for small x:* $t \to Ux$ *or* $U \to t/x$
- *correlated* variables *e.g.* $t \ll U \ll \Delta$ *- order of two series for* $t \ll U$ *and* $U \ll \Delta$ *matters (limit does not exist)*

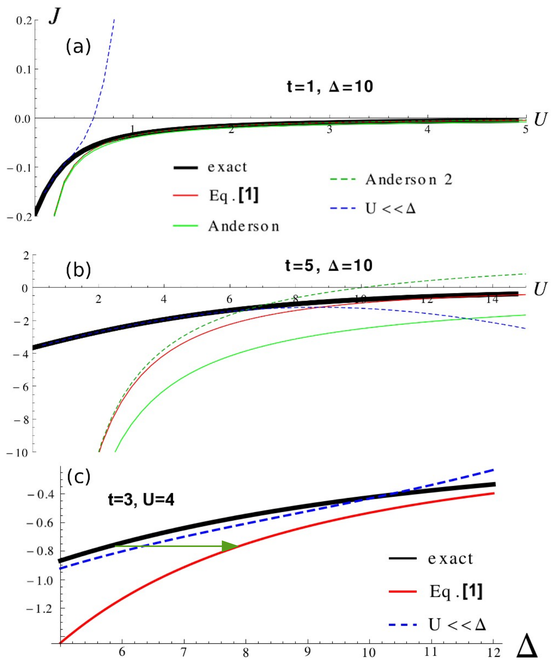
Mott-Hubbard insulator $t < U < \Delta$



Results

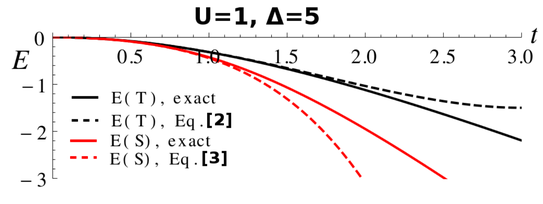
The expansion for $t \ll U$ using $t \to Ux$ yields $J = \dfrac{-4(\Delta+2U)t^4}{U(\Delta+U)^3} + O(x^6)$ **[1]**

Further expansion for $U \ll \Delta$ yields $J_{Anderson} = \dfrac{J_{dir}t^2}{\Delta^2}$ for $J_{dir} = -4t^2/U$ or $J_{Anderson\ 2} = \dfrac{4t^4(U-\Delta)}{\Delta^3 U}$ depending on the expansion procedure



- Order of expansions matters: starting from $U \ll \Delta$ does not give the "Anderson" result
- From (a) we see that $U<t$ can give excellent agreement with the exact result
- A measured value of $J=-3.5$ is obtained in (b) by $U=7.1$ for the Anderson result, vs $U=0.3$ for the exact result, which places it out of the Mott-Hubbard insulator picture
- Materials can thus be characterized fictitiously as Mott-Hubbard insulators when the parameter relationships are "mild": $t \lesssim U \lesssim \Delta$
- From (c) we see how **[1]** can be deceptive, with Δ quantitatively incorrect
- Formula **[1]** also arises from other, parameter-dependent expansions, *e.g.* $x=t^2/(U\Delta)$ where either U or Δ may be small (*e.g.* $<t$)
- Thus, the limits $t \ll U \ll \Delta$, which arise from the use of perturbation theory, represent a subset of the applicability of the limiting form for J

Radii of convergence



- Again results in Eq. **[1]** for J
- Convergence condition for infinite order in x^*: $t<2.1$ for $E(T)$ and $t<1.3$ for $E(S)$

$$E(T) = \frac{1}{2}\left(\Delta + U - \sqrt{\Delta^2 + 2\Delta U + 8t^2 + U^2}\right)$$

expanding with $x^*=t/(U+\Delta)$ gives *parameter-free* radius of convergence only for *E(T)*: $x^*<0.36$

$$E(T) = -\frac{2t^2}{U+\Delta} + \frac{4t^4}{(U+\Delta)^3} + \cdots \quad \textbf{[2]}$$

$$E(S) = -\frac{2t^2}{U+\Delta} - \frac{4t^4}{U(U+\Delta)^2} + \cdots \quad \textbf{[3]}$$

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