Superexchange in Mott-Hubbard Insulators

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We discuss the well-known three-center cation-anion-cation model for superexchange in insulating transition-metal compounds using limiting expansions for the Anderson-Hubbard model. We find that due to the three interfering energy scales in the model, a limiting expression for the superexchange $J$ for the idealized Mott-Hubbard (M-H) case $t \ll U \ll \Delta$ cannot be formally defined. We find that no single expansion variable can describe any type of limiting behaviour for superexchange. The well-known $t^4$ expression for M-H insulators, obtained from path-dependent series expansions, is not unique to these systems as it can also be obtained with other different, also non-convergent expansions, in which either the $p-d$ energy difference $\Delta$ or the $d$-electron correlation $U$ can actually be small. At times, and particularly for milder relationships between the parameters, $t \lesssim U \lesssim \Delta$, the reverse form of the series expansions can yield better agreement with the exact results. This implies that the fitting of experimental data to the simple expressions can lead to qualitatively incorrect values for the parameters, fictitiously within the Mott-Hubbard regime.

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The problem of superexchange, or the interaction at a distance of two electron spins, dates back e.g. to the work of Anderson [1] who obtained a simple expression for describing the interaction of 3$d$ spins in Mn atoms separated by a filled shell of O 2$p$ electrons, and since then the concept has been applied to the estimation of parameters in a wide variety of systems, such as hopping parameters in transition-metal compounds [2, 3], high $T_c$ superconductors [4], and to electron transfer rates in donor-acceptor systems, such as radical pairs in biological molecules [5]. Following Anderson, many works in the literature have presented slight modifications of the superexchange expression $J$ [6–9]. Experimentally, the electronic parameters cannot be measured directly. Some experimental works rely on assumed models for exchange in order to fit spin-wave measurements [10], and are therefore biased by the suitability of the model while some others, for example, which fit photoemission spectra to parameters from cluster models [11], constitute an independent approach to obtaining values for the electronic parameters.

Obtaining a simple expression for complex quantities often relies on series expansions. A careful examination of the convergence properties of the expansion is necessary when there are multiple scales in the problem. Bender [12] has recently revisited the problem of multiple, correlated energy scales in terms of $\mathcal{PT}$ symmetry while a recent study [13] has found that no single expansion variable can describe any type of limiting behaviour for superexchange. The well-known $t^4$ expression for M-H insulators, obtained from path-dependent series expansions, is not unique to these systems as it can also be obtained with other different, also non-convergent expansions, in which either the $p-d$ energy difference $\Delta$ or the $d$-electron correlation $U$ can actually be small. At times, and particularly for milder relationships between the parameters, $t \lesssim U \lesssim \Delta$, the reverse form of the series expansions can yield better agreement with the exact results. This implies that the fitting of experimental data to the simple expressions can lead to qualitatively incorrect values for the parameters, fictitiously within the Mott-Hubbard regime.

The Anderson-Hubbard Hamiltonian in second-quantized form is given by

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

where $\langle i, j \rangle$ denotes that the hopping with energy $t$ is restricted to nearest neighbours, the $\epsilon_i$ term describes the on-site energy of an electron, and $n_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$ is the number of electrons of spin $\sigma$ on site $i$. The presence of two electrons of opposite spin on a site comes at an energy cost $U$ due to Coulomb repulsion.

We specifically consider the Wannier-orbital representation of Anderson’s model of the MnO crystal, where in the ground state, unpaired 3$d$ electrons on Mn are separated by O with a filled 2$p$-shell, as in Fig. 1. Here, the $p-d$ energy difference, $\epsilon_p - \epsilon_d$ has been defined as $\Delta$. The Hamiltonian has been split into tri-diagonal block form:

$$H = \begin{pmatrix}
H_{00} & T_{01} & 0 \\
T_{10} & H_{11} & T_{12} \\
0 & T_{21} & H_{22}
\end{pmatrix}$$

(2)
energy eigenvalues for $U \gg t$ up to $O(t^4)$ is
\[ E(T) = \left( \frac{2\Delta^4}{U^4} - \frac{2\Delta^2}{U^2} + \frac{2\Delta}{U} - \frac{2}{U} \right) t^2 + \left( \frac{4}{U^3} - \frac{12\Delta}{U^4} \right) t^4 \]
\[ E(S) = \left( \frac{2\Delta^4}{U^4} - \frac{2\Delta^2}{U^2} + \frac{2\Delta}{U} - \frac{2}{U} \right) t^2 + \left( \frac{8\Delta}{U^4} - \frac{4}{U^3} \right) t^4 \]
such that
\[ J = \frac{4t^4(5\Delta - 2U)}{U^4}. \]

Eqs. 6-7 were derived by substituting for $U \rightarrow t/x$ and expanding about $x$, and the same result is obtained for $U \rightarrow \infty$ for $O(1/U^4)$ (single-scale limit).

On the other hand, setting $t \rightarrow UX$ gives a totally different result:
\[ J = -\frac{4(\Delta + 2U)t^4}{(\Delta + 2U)^2}, \]
a result also obtained from the exact $J$ by the single-scale series expansion $t \to 0$. The result is widely used for the $t << U$ situation e.g. Ref. 2, Eq. 13 and Ref. 11 Eq. 16, and it is often used as is, as it can describe either the Mott-Hubbard (M-H) case $\Delta > U$ [2, 3, 7], or the charge-transfer limit $\Delta < U$ [11, 17] without further, unrealistic limits relating $\Delta$ to $U$ considered.

In deriving Eqs. 6-7, no assumptions have been made for $\Delta$ and yet, Eq. 7 poorly represents the exact $J$ for $\Delta > t$ as it increases without bound whereas the exact $J$ approaches zero as $\Delta$ is increased because higher-order in $t$ terms are needed for convergence except for the trivial case $U = \infty$ where it's equal to zero. On the other hand, the expansion leading to Eq. 8 converges for all $\Delta$ but is better for larger $\Delta$.

The formalism of the effective Hamiltonian was invoked here in order to compare the results with its usual implementation, involving setting the unknown energy $E$ in Eqs. 4-5 equal to the unperturbed energy of the energetically degenerate basis functions in the model basis. If this is done, then the value of the exchange is
\[ J = \frac{-4t^4(\Delta + 2U)}{(\Delta + U)(\Delta^2 + 2\Delta(U^2 - t^2) - 4t^2U + U^3)}. \]
whence Eq. 7 or 8 is obtained upon setting $U \rightarrow t/x$ or $t \rightarrow UX$ respectively and expanding about $x \equiv t/U$ (or by defining $x = t/\Delta$). On the other hand, taking the series expansion $U \ll \Delta$ of Eq. 9 does not
lead to the results presented in Fig. 2, for the $U \ll \Delta$ limit of the exact $J$; the validity of the perturbation expansion requires that $t$ be much smaller than all of the other energy scales in the problem and the convergence of $U \ll \Delta$ is mostly incongruent with this.

The usual “Anderson” expression for superexchange\textsuperscript{11} can be derived by considering the $U \ll \Delta$ limit of expression 8, yielding, in terms of the direct-exchange term connecting $d-d$ nearest neighbours: $J_{\text{dir}} = -4t^2/U$:

$$J_{\text{Anderson}} = \frac{J_{\text{dir}} t^2}{\Delta^2}. \quad (10)$$

Eq. 10 was obtained with $\Delta \to U/x$ and expanding about $x$ and $U \to \Delta x$ yields the modified expression,

$$J_{\text{Anderson} 2} = \frac{4t^4(U - \Delta)}{\Delta^4 U} \quad (11)$$

which differs from Eq. 10 by one order of expansion.

We focus on the expansion obtained by setting $U \to \Delta x$ before expanding in $x$. For large $t$ it is accurate, but for small $t$ it diverges for all but the smallest values of $U$ as can be seen from Fig. 2. This shows explicitly how the parameter-dependence of the $U/\Delta$ expansion in terms of $U/\Delta$. The $t \ll U$ expansion (Eq. 8) is also shown for comparison, even though it is not expected to hold for $t \gtrsim U$. Extrapolating beyond (c) for even larger $t$ the $U/\Delta$ expansion is very accurate, even for $U > \Delta$.

If the limits $U \ll \Delta$ and $t \ll U$ were in fact interchangeable, then Eq. 11 which was derived in exactly the same manner, should agree with the $U \ll \Delta$ curve for the larger values of $U$, particularly in Fig. 2a. Neither in the charge-transfer insulator $t \ll \Delta \ll U$ situation, do the limits commute.

The limiting forms Eqs. 8, 10, 11 provided that $t \ll U \ll \Delta$ is strictly adhered to, lead to an accurate result for $J$. Where the limiting forms of Anderson or Eq. 8 are worse than the $U \ll \Delta$ expression are for cases in which the milder relationship $t \lesssim U \lesssim \Delta$ holds. For instance in Fig. 2, a value of $J = -3.5$ is obtained by $U = 7.1, 4.5$, and 0.3 for the Anderson, Eq. 8, and $U \ll \Delta$ expressions respectively, causing the M-H relationship $t < U < \Delta$ to be fictitiously satisfied. Similarly, for Fig. 2b, for a measured $J = -0.3$, the values are $U = 5.2, 3.9$, and 3.1 respectively, such that the qualitative relationship $t < U < \Delta$ is correctly determined, but with an inaccurate $U$ in the M-H model.

Fig. 3 shows another perspective, that for $t \lesssim U$ the fitting of $J$ to the model of Eq. 8 as opposed to the $U \ll \Delta$ limiting form, can give a value for $\Delta$ much larger than the correct one.

![Fig. 2](image1)

**Fig. 2.** The variation of $J$ with $U$ for fixed $\Delta$ and different values of $t$, in the exact form and in the limiting cases $t \ll U$ (Eq. 8), the $U \ll \Delta$ limit of $t \ll U$ (“Anderson” case, Eq. 10) and “Anderson 2” (Eq. 11), and $U \ll \Delta$ as discussed in the text.

![Fig. 3](image2)

**Fig. 3.** the variation of $J$ with $\Delta$ for $t = 3, U = 4$, in the exact form and in the limiting cases Eq. 8 and $U \ll \Delta$.

Setting $x \to tU$ followed by $y \to U\Delta$, and expanding in $x$ and $y$ simultaneously yields zero up to and including at least fourth order in $x = t/U$ and $y = U/\Delta$ (using Mathematica\textsuperscript{15}), yielding finally zero up to fourth order in $t$. The disagreement in the
result between the sequence in which the expansions are taken, either separately or simultaneously, means that the limit is formally undefined. This manifests itself as a better agreement of the $U \ll \Delta$ expression with the exact result for the milder limits compared with the results derived starting with $t \ll U$, due to a divergence of the latter with increasing order in the expansion in this region (Fig. 4).

The inconsistency between the two types of expansion procedures (e.g. leading to Eqs. 7 and 8 respectively) is due to the radius of convergence (ROC) being unstable due to the multiple variables and due to the fractional powers present in the function. Considering the triplet energy, which has the simple form

$$E(T) = \frac{1}{2} \left( \Delta + U - \sqrt{\Delta^2 + 2\Delta U + 8t^2 + U^2} \right). \quad (12)$$

Substituting for $t$ as $t \to \Delta U$ yields one form for the series, and another form with $U \to t/\Delta$. The first form has a ROC which is dependent on $\frac{U+\Delta}{U^2}$, while in the second form there was an unstable parameter dependence with increasing series order. The ROC of both forms coincide and are parameter-free when $\Delta = 0$. Parameter-dependent ROC require that an additional condition be satisfied; in this case this condition is looser than that of the smallness of the expansion parameter and together they yield an expansion variable which gives a parameter-free ROC $x = t/(\Delta + U)$, for $E(T)$ which converges for $t/(U+\Delta) \lesssim 0.36$. Incidentally, several other forms of the expansion variable, for example $x = t^2/(U\Delta)$, when combined with the convergence condition for $E(T)$ also give the same condition. In the case of the singlet however, the ROC remains parameter-dependent and more restrictive. Up to fourth order in the expansion parameter, we have derived the expressions:

$$E(T) = -\frac{2t^2}{U+\Delta} + \frac{4t^4}{(U+\Delta)^3}, \quad (13)$$

$$E(S) = -\frac{2t^2}{U+\Delta} - \frac{4t^4}{U(U+\Delta)^2}, \quad (14)$$

which result again in Eq. 8 for $J$, a ubiquitous expression also obtained with some other expansion parameters, such as $x = t^2/(U\Delta)$. For $U = 1$, $\Delta = 10$ it gave $t/(U+\Delta) \lesssim 0.18$, or $t < 2$, compared with $t < 3.9$ for the triplet. Thus, $U$ need not be larger than $t$ for Eq. 8 to be accurate (see also Fig. 2a for this case). Fig. 5 shows the difference in the convergence for $U = 1$ and $\Delta = 5$ for which the numerical evaluation gave $t < 2.1$ and $t < 1.4$ for $E(T)$ and $E(S)$ respectively. Clearly, $J$ is composed of two functions with different convergence properties.

We have shown that the commonly referred-to Mott-Hubbard (M-H) insulator situation, $t \ll U \ll \Delta$ yields the Anderson form for superexchange if the limits are taken in a particular sequence, while the combined series expansion is zero up to the $O(t^4)$ given in the Anderson expression. Hence, the limit is actually undefined (also true for the charge-transfer insulator) and the reason for this is the incongruence of the expansion variables with the radius of convergence, which depends on the parameters of the problem. The Anderson expression or simply the limiting expressions, derived e.g. from $t \ll U$, but also from many other parameter relationships, agree very well with the exact result in the extreme form of these limits; for milder relationships between the parameters, e.g. $t < U < \Delta$, the limiting form can be significantly less accurate than oppositely-derived limit $U \ll \Delta$.

The M-H limits, which arise from the convenience of perturbation theory, represent a subset of the
range of applicability of the limiting form as we found that other expansions, which assume different relationships between the variables, e.g. \( U < t \), yield the same limiting form to \( J \) to great success. We additionally show that since the triplet and singlet energies comprising \( J \) display different convergence properties, which nonetheless overlap reasonably well for material parameters located, say, within an order of magnitude of each other, a single expansion variable for determining \( J \) does not formally exist.

The wider implications of our findings are that the results determined for electron transfer rates, or other internal parameters, could be questionable if an expression of a similar type as \( J \) is relied upon as the parameters found from such experiments (such as the fitting of spin-wave results \([10]\)) could be outside the radius of convergence of the series, particularly when the parameters do not hold extreme relationships amongst themselves, yielding a fictitious qualitative relationship between the parameters.

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