Charge transfer: two-level system

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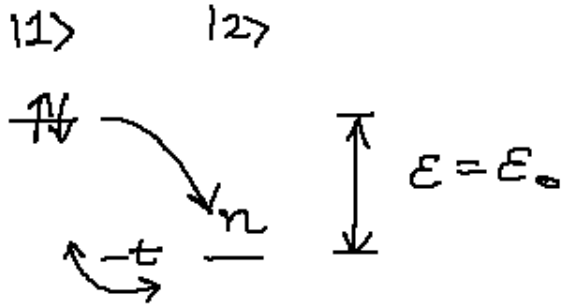
February 25, 2014

Here we study a simple model of charge transfer using a two-level system to see the behavior of the most elementary quantum system with some covalence. We will first study the actual man-body system and then the single-particle version of it which shows some serious deficiencies. For the single-particle version, we have charge transfer from one state to another and this changes their relative energies (i.e. creates a potential difference) which seems physical at first but can create seriously bad predictions.

1 Many-body version

We have systems 1 and 2, and for each we have one electronic level of interest called $|1\rangle$ and $|2\rangle$. The systems start far apart so they do not interact. State $|1\rangle$ initially has two electrons (full occupation) and state $|2\rangle$ is empty. The interesting level alignment is when the energy of $|1\rangle$ is initially higher than that of $|2\rangle$ and we want to know what happens when they come into contact. (For simplicity, we assume the states are orthogonal.) The state $|2\rangle$ is quite localized and has a sizable Hubbard U.



The many-body Hamiltonian is then

$$\hat{H} = -\epsilon_0 \hat{n}_2 - t \sum_\sigma \left(\hat{c}^\dagger_{1\sigma} \hat{c}_{2\sigma} + \hat{c}^\dagger_{2\sigma} \hat{c}_{1\sigma} \right) + U \hat{n}_{2\uparrow} \hat{n}_{2\downarrow}$$

where σ is spin $\uparrow$ or $\downarrow$, $\hat{n}_i = \sum_\sigma \hat{n}_{i\sigma}$ and $\hat{n}_{i\sigma} = \hat{c}^\dagger_{i\sigma}\hat{c}_{i\sigma}$.

For $t = 0$, the eigenstates are (i) $|\uparrow\downarrow, 0\rangle$ with energy 0, (ii) triplet $|\uparrow,\uparrow\rangle$, $(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle)/\sqrt{2}$, and $|\downarrow,\downarrow\rangle$ with energy $-\epsilon_0$, (iii) singlet $(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle)/\sqrt{2}$ with energy $-\epsilon_0$, and (iv) $|0,\uparrow\downarrow\rangle$ with energy $-2\epsilon_0 + U$.

When we have $t \neq 0$, the triplet states are unaffected but the three spin zero states couple so we get a 3×3 problem. In the basis ordered $\{(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle)/\sqrt{2},\ |\uparrow\downarrow, 0\rangle,\ |0,\uparrow\downarrow\rangle\}$ the Hamiltonian is the matrix

$$H_{S=0} = \begin{pmatrix} -\epsilon_0 & -\sqrt{2}t & -\sqrt{2}t \\ -\sqrt{2}t & 0 & 0 \\ -\sqrt{2}t & 0 & U - 2\epsilon_0 \end{pmatrix}$$

The solutions are very messy but of course doable analytically since we have a cubic problem. First, we get a qualitative idea by looking at some extreme cases for what the ground state $|\Psi_0\rangle$ looks like

$$\begin{array}{lcl} |t| \to \infty & \to & |\Psi_0\rangle = \text{strong covalence, mixture of all three states} \\ U \to \infty & \to & |\Psi_0\rangle = a(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle)/\sqrt{2}) + b|\uparrow\downarrow, 0\rangle \text{ where } |a| > |b| \\ |t| \to 0 \text{ and } U > \epsilon_0 & \to & |\Psi_0\rangle \approx \frac{1}{\sqrt{2}}\left(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\right) \\ |t| \to 0 \text{ and } U < \epsilon_0 & \to & |\Psi_0\rangle \approx |0,\uparrow\downarrow\rangle \\ |t| \to 0 \text{ and } U = \epsilon_0 & \to & |\Psi_0\rangle \approx \frac{1}{2}\left(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\right) + \frac{1}{\sqrt{2}}|0,\uparrow\downarrow\rangle \end{array}$$

Let's consider the case of relatively large U so $U > \epsilon_0$ which simply means that at $t = 0$, the ground state does not have two electrons on the second state (due to the $-\epsilon_0$) but instead has put one on each site. In the perturbative limit of small t (specifically $|t| \ll \epsilon_0$ and $U - \epsilon_0$), the ground state energy is

$$E_0 = -\epsilon_0 - \frac{2t^2}{\epsilon_0} - \frac{2t^2}{U - \epsilon_0} + O(t^4)$$

and unnormalized wave function is

$$|\tilde{\Psi}_0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\right) + \frac{\sqrt{2}t}{\epsilon_0}|\uparrow\downarrow, 0\rangle\frac{\sqrt{2}t}{\epsilon_0} + \frac{\sqrt{2}t}{U - \epsilon_0}|0,\uparrow\downarrow\rangle + O(t^2)$$

and normalized wave function is

$$|\Psi_0\rangle = \left(1 + \frac{2t^2}{\epsilon_0^2} + \frac{2t^2}{(U - \epsilon_0)^2}\right)^{-1/2}|\tilde{\Psi}_0\rangle + O(t^3)$$

and the occupancy of site $|2\rangle$ is

$$\langle\hat{n}_2\rangle = \frac{1 + 2[2t^2/(U - \epsilon_0)^2]}{1 + 2t^2/\epsilon_0^2 + 2t^2/(U - \epsilon_0)^2} + O(t^3) = 1 - \frac{2t^2}{\epsilon_0^2} + \frac{2t^2}{(U - \epsilon_0)^2} + O(t^3)$$

The main points are (i) for $t = 0$, the occupancy of site $|2\rangle$ is one electron when $U > \epsilon_0$; (ii) for $t \neq 0$ but small, the occupancy is still close but whether it is larger or smaller depends on

how large $U-\epsilon_0$ is compared to ϵ_0: the double occupancy of $|1\rangle$ reduces $\langle\hat{n}_2\rangle$ while double occupancy of $|2\rangle$ increases it; and (iii) the behavior versus t is quite smooth as we expect from perturbation theory: we can send $U\to\infty$ and $\langle\hat{n}_2\rangle$ stays reasonable and close to one for $|t/\epsilon_0|\ll 1$.

Here is a table of numerical solutions for $\langle\hat{n}_2\rangle$ as a function of t/ϵ_0 and U/ϵ_0:

	U/ϵ_0				
t/ϵ_0	0	0.25	1.1	2	3
0	2.0000	2.0000	1.0000	1.0000	1.0000
0.25	1.8944	1.8380	1.3133	1.0000	0.9415
1	1.4472	1.3817	1.1680	1.0000	0.8867
2	1.2425	1.2075	1.0974	1.0000	0.9155
3	1.1644	1.1414	1.0682	1.0000	0.9356

2 Single-particle version

We begin by computing the expectation of the Hamiltonian under the approximation that we can factorize the interaction

$$\langle\hat{H}\rangle \approx -\epsilon_0\langle\hat{n}_2\rangle - t\sum_\sigma\left(\langle\hat{c}^\dagger_{1\sigma}\hat{c}_{2\sigma}+\hat{c}^\dagger_{2\sigma}\hat{c}_{1\sigma}\rangle\right)+U\langle\hat{n}_{2\uparrow}\rangle\langle\hat{n}_{2\downarrow}\rangle\,.$$

We simplify notation by defining the occupancy numbers (expectations) $n_{i\sigma}\equiv\langle\hat{n}_{i\sigma}\rangle$ so

$$\langle\hat{H}\rangle \approx -\epsilon_0 n_2 - t\sum_\sigma\left(\langle\hat{c}^\dagger_{1\sigma}\hat{c}_{2\sigma}+\hat{c}^\dagger_{2\sigma}\hat{c}_{1\sigma}\rangle\right)+Un_{2\uparrow}n_{2\downarrow}\,.$$

This is a non-linear self-consistent single-particle problem. We are looking for an optimal single-particle description with lowest energy expectation. Taking variational derivatives of $\langle\hat{H}\rangle$ versus single-particle wave functions $\psi_{i\sigma}$ gives us the single-particle Hamiltonian matrices h_σ for each spin in the $|1\rangle,|2\rangle$ basis

$$h_\sigma = \begin{pmatrix} 0 & -t \\ -t & -\epsilon_0+Un_{2,-\sigma}\end{pmatrix}$$

We get two standard 2×2 problems where $h_\uparrow$ depends on $n_{2,\downarrow}$ and vice versa. We can easily solve the two 2×2 problems. The matrix h_σ has eigenvalues

$$E_{\sigma,\pm} = -\frac{\epsilon_0-Un_{2,-\sigma}}{2}\pm\sqrt{t^2+\left(\frac{\epsilon_0-Un_{2,-\sigma}}{2}\right)^2}$$

and eigenvectors

$$v_{\sigma,+}=\begin{pmatrix}\cos(\theta/2)\\ \sin(\theta/2)\end{pmatrix}\quad,\quad v_{\sigma,-}=\begin{pmatrix}-\sin(\theta/2)\\ \cos(\theta/2)\end{pmatrix}$$

where

$$\cos(\theta) = \frac{(\epsilon_0 - U n_{2,-\sigma})/2}{\sqrt{t^2 + ((\epsilon_0 - U n_{2,-\sigma})/2)^2}} \quad , \quad \sin(\theta) = \frac{-t}{\sqrt{t^2 + ((\epsilon_0 - U n_{2,-\sigma})/2)^2}}$$

Since we have two electrons, there are two possibilities for the ground state. First, it could be that both electrons have the same spin, say $\uparrow$. This would mean both eigenvalues of $h_\uparrow$ are lower than both of $h_\downarrow$. So we have $n_{2,\uparrow} = 1$ and $n_{2,\downarrow} = 0$. The condition $E_{\uparrow,+} < E_{\downarrow,-}$ translates into

$$-\frac{\epsilon_0}{2} + \sqrt{t^2 + (\epsilon_0/2)^2} = E_{\uparrow,+} < E_{\downarrow,-} = -\frac{\epsilon_0 - U}{2} - \sqrt{t^2 + \left(\frac{\epsilon_0 - U}{2}\right)^2}$$

or

$$\sqrt{t^2 + (\epsilon_0/2)^2} + \sqrt{t^2 + (U/2 - \epsilon_0/2)^2} < U/2$$

This is actually impossible to fulfill[1] so it just says the triplet states are not the ground state! But notice that the triplets are described perfectly by this single-particle approach since their total energies are exactly $-\epsilon_0$ and their wave functions are single Slater determinants which are the same as the exact wave function for triplets.

The second and only remaining possibility is that we fill one state of each spin for net spin projection zero along z. Namely, we fill one bonding state for spin up and one bonding state for spin down. The self-consistency condition is then

$$n_{2,\sigma} = \frac{1}{2}\left(1 + \frac{\epsilon_0 - U n_{2,-\sigma}}{\sqrt{4t^2 + (\epsilon_0 - U n_{2,-\sigma})^2}}\right) .$$

If we define

$$f(x) \equiv \frac{1}{2}\left(1 + \frac{\epsilon_0/t - xU/t}{\sqrt{4 + (\epsilon_0/t - xU/t)^2}}\right)$$

then we wish to find

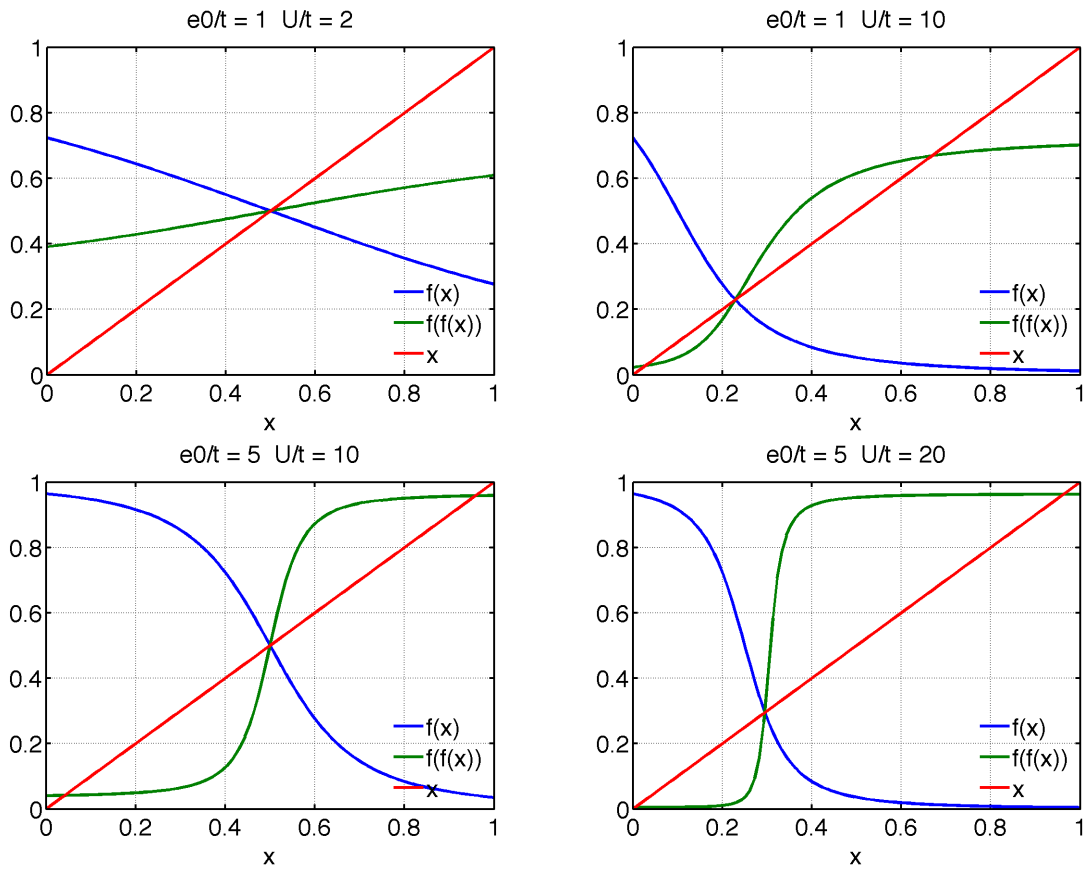
$$n_{2,\sigma} = f(n_{2,-\sigma}) \quad , \quad n_{2,-\sigma} = f(n_{2,\sigma})$$

which is the same as finding solutions to

$$n_{2,\sigma} = f(f(n_{2,\sigma})) .$$

Solving the algebraic equation $x = f(f(x))$ for $0 \leq x \leq 1$ is messy enough of a quartic equation that we have to solve it graphically and numerically. Below are some representative plots of x, $f(x)$, and $f(f(x))$ for various choices of parameters ϵ_0/t and U/t: When U is small enough, we get only one unique solution to $x = f(x)$ which means equal up and down spins (paramagnetic solution) $n_{2,\sigma} = n_{2,-\sigma}$). For larger U, we get three solutions: one paramagnetic $x = f(x)$ and two distinct high/low spin ones where $x \neq f(x)$ but $x = f(f(x))$. For the latter, if we choose $n_{2,\uparrow}$ to be larger, then $n_{2,\downarrow} = f(n_{2,\uparrow}) < n_{2,\uparrow}$.

[1]The impossibility is easily seen via geometry. Let $U = x + \epsilon_0$ and then the inequality is basically saying that the hypotenuse of a right triangle is shorter than one side.



We end up with a symmetric paramagnetic solution and a symmetry breaking spin-polarized solution roughly like an antiferromagnetic solution but not precisely as we don't have symmetry between the sites (due to ϵ_0 and U only being on site 2). The table below gives some numerical values

ϵ_0/t	U/t	Paramagnetic solution $n_{2,\sigma}$	Spin-polarized $n_{2,\sigma}$ values
0.1	0.05	0.52	–
0.1	0.2	0.50	–
0.1	5	0.25	–
0.1	10	0.18	0.06 / 0.38
1	1	0.60	–
1	2	0.50	–
1	5	0.34	0.20 / 0.50
1	10	0.23	0.03 / 0.67
2	2	0.66	–
2	4	0.50	–
2	5	0.44	0.17 / 0.75
2	8	0.34	0.04 / 0.82
2	20	0.18	0.004 / 0.85
5	20	0.30	0.005 / 0.96
12	20	0.58	0.02 / 0.99

As expected, we find that for large enough U, the system spin-polarizes to avoid double-occupancy so that the paramagnetic solution is higher in energy and the spin-polarized solution is the ground state.

Let us look at the perturbative case of t being very small compared to ϵ_0 and U. Furthermore, we will take $U > \epsilon_0$. Then $f(0) \approx 1$ and $f(1) \approx 0$. We always have that $f(\epsilon_0/U) = 1/2$ so the transition between 1 and 0 for f will happens over a narrow range of x on the order of t/U around $x = \epsilon_0/U$. So the paramagnetic solution has $n_2 \approx \epsilon_0/U$ while the spin-polarized solutions have $n_{2,\sigma}$ values close to 1 and 0. For x not close to ϵ_0/U, we have the Taylor series

$$f(x) = \frac{1}{2}\left(1 + \frac{\mathrm{sgn}(\epsilon_0 - Ux)}{\sqrt{1 + \frac{4t^2}{(\epsilon_0 - Ux)^2}}}\right) = \frac{1}{2}\left(1 + \mathrm{sgn}(\epsilon_0 - Ux) - \frac{2t^2 \mathrm{sgn}(\epsilon_0 - Ux)}{(\epsilon_0 - Ux)^2} + \ldots\right)$$

so we get in the perturbative regime

$$n_{2,\uparrow} = f(0) \approx 1 - \frac{t^2}{\epsilon_0^2} \quad , \quad n_{2,\downarrow} = f(1) \approx \frac{t^2}{(U - \epsilon_0)^2}$$

and so

$$n_2 = 1 - \frac{t^2}{\epsilon_0^2} + \frac{t^2}{(U - \epsilon_0)^2} + O(t^3)$$

which has the correct form perturbative form compared to the exact value but off by a factor of two for the correction to unity.

Before we analyze these results in comparison to the right answer, we digress to see how this single-particle theory behaves for the paramagnetic solution which is technically interesting if physically wrong. In the paramagnetic case, both spin solutions are degenerate so we just have a single self-consistent problem where $n_{2,\sigma} = n_{2,-\sigma}$. When $t = 0$, if $n_{2,\sigma} = 0$ then this means electrons want to go to site 2; but if $n_{2,\sigma} = 1$ and $U > \epsilon_0$, then this would push level 2 above level 1. For large U, what happens is a small number of electrons $2n_{2,\sigma} = 2\epsilon_0/U$ transfer from site 1 to site 2 which raises the energy of site 2 to zero energy and this completes the charge transfer because the two sites are then degenerate in energy.

For $t > 0$ but still small, here is a numerical example to give a flavor: for $\epsilon_0/t = 3$ and $U/t = 10$ we get $n_{2,\sigma} = 0.36$ and the two eigenstates

$$\begin{aligned} |E_{low} = -0.75\rangle &= +0.80|1\rangle + 0.60|2\rangle \quad \text{doubly-occupied} \\ |E_{high} = +1.34\rangle &= -0.60|1\rangle + 0.80|2\rangle \quad \text{empty} \end{aligned}$$

Interestingly, the occupied state is mainly on site 1 and not on site 2: the electron transfer $n_{2,\sigma} = 0.36$ has raised the energy of site 2 high enough above zero to make it less occupied that site 1. So the effect of covalency $t \neq 0$ is to break the degeneracy of charge transfer equilibrium for $t = 0$ and raise the energy of the accepting site to be consistent with the final small charge transfer. For the same parameters, the spin polarized solution has $n_{2,\uparrow} = 0.904$

and $n_{2,\downarrow} = 0.025$ with

$$\begin{aligned} |E_{low,\uparrow} = -3.07\rangle &= +0.31|1\rangle + 0.95|2\rangle \\ |E_{low,\downarrow} = -0.16\rangle &= +0.99|1\rangle + 0.16|2\rangle \\ |E_{high,\uparrow} = +0.33\rangle &= -0.95|1\rangle + 0.31|2\rangle \\ |E_{high,\downarrow} = +6.20\rangle &= -0.16|1\rangle + 0.99|2\rangle \end{aligned}$$

Now let us discuss the physics. Physically, the paramagnetic solution is wrong for large U since it predicts a finite electron transfer $2n_2 \approx 2\epsilon_0/U$ independent of t for small t which does not go to zero as it should. The mean-field approach treats electrons as some continuous fluid that can have fractional densities: with fractional transfer, we raise the energy of site 2 by some desired amount to align it with ϵ_0. But the real system has real discrete electrons: either there is no electron, one electron, or two electrons on site 2; when there are two, the energy is higher by the big number U; there is no sense of scaling up to intermediate U by some intermediate number of electrons (even if the expectation value $\langle \hat{n}_2 \rangle$ is fractional). Basically, n_2 fluctuates between 0, 1, and 2, and we get big changes of energy: fluctuations matter a great deal which we can't incorporate in a simple mean-field approach.

The spin-polarized solution makes the electrons avoid each other by localizing them on different sites, but it does this by using the spin quantum number as a lever. By wrongly breaking spin symmetry, it makes eigenstates of one spin localize on one site and of the other spin on the other site. The actual answer of course has zero spin and zero spin polarization, so this is also physically wrong. But at least it is reasonable.