Computing spin correlations with 2-body density matrix and other misc notes

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Operators are written like variables for simplicity. What is or isn't an operator should be clear from context.

1 Computing spin correlations with 2-body density matrix

The prerequisites are that

$$S_\pm = S_x \pm iS_y, \qquad S_z = \frac{1}{2}(c_\uparrow^\dagger c_\uparrow - c_\downarrow^\dagger c_\downarrow) \tag{1}$$

which can be found by Wikipedia, looking for "spin operator". Using this,

$$S_x = \frac{1}{2}(S_+ + S_-) \qquad S_y = \frac{1}{2i}(S_+ - S_-) \tag{2}$$

You can also derive this by taking $S_\alpha = c_\sigma^\dagger \tau_{\alpha,\sigma\sigma'} c_{\sigma'}$, where $\tau_{\alpha,\sigma\sigma'}$ are the Pauli matrices.

The rest is careful algebra after plugging these in.

$$\begin{aligned}
S_i \cdot S_j &= S_{ix}S_{jx} + S_{iy}S_{jy} + S_{iz}S_{jz} && (3)\\
&= \frac{1}{2}(S_{i+}S_{j-} + S_{i-}S_{j+}) + S_{iz}S_{jz} && (4)\\
&= \frac{1}{2}\left(c_{i\uparrow}^\dagger c_{i\downarrow} c_{j\downarrow}^\dagger c_{j\uparrow} + c_{i\downarrow}^\dagger c_{i\uparrow} c_{j\uparrow}^\dagger c_{j\downarrow}\right) + \frac{1}{4}\left(c_{i\uparrow}^\dagger c_{i\uparrow} c_{j\uparrow}^\dagger c_{j\uparrow} + c_{i\downarrow}^\dagger c_{i\downarrow} c_{j\downarrow}^\dagger c_{j\downarrow} - c_{i\downarrow}^\dagger c_{i\downarrow} c_{j\uparrow}^\dagger c_{j\uparrow} - c_{i\uparrow}^\dagger c_{i\uparrow} c_{j\downarrow}^\dagger c_{j\downarrow}\right) && (5)\\
&= -\frac{1}{2}\left(c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger c_{i\downarrow} c_{j\uparrow} + c_{j\uparrow}^\dagger c_{i\downarrow}^\dagger c_{j\downarrow} c_{i\uparrow}\right) - \frac{1}{4}\left(c_{i\uparrow}^\dagger c_{j\uparrow}^\dagger c_{i\uparrow} c_{j\uparrow} + c_{i\downarrow}^\dagger c_{j\downarrow}^\dagger c_{i\downarrow} c_{j\downarrow} + c_{j\uparrow}^\dagger c_{i\downarrow}^\dagger c_{i\downarrow} c_{j\uparrow} + c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger c_{j\downarrow} c_{i\uparrow}\right) && (6)
\end{aligned}$$

The last step is rearranging the operators according to the chemistry notation (8). Using that notation,

$$S_i \cdot S_j = -\frac{1}{2}\left(\rho_{ijji}^{\uparrow\downarrow} + \rho_{jiij}^{\uparrow\downarrow}\right) - \frac{1}{4}\left(\rho_{ijji}^{\uparrow\uparrow} + \rho_{ijji}^{\downarrow\downarrow} + \rho_{jjii}^{\uparrow\downarrow} + \rho_{iijj}^{\uparrow\downarrow}\right) \tag{7}$$

2 Misc notes when working on this

`PySCF` uses the "chemistry notation" when storing the 2-body density matrix. In particular,

$$\rho_{ijkl}^{\uparrow\downarrow} = \langle c_{i\uparrow}^\dagger c_{k\downarrow}^\dagger c_{l\downarrow} c_{j\uparrow}\rangle \tag{8}$$

This is documented in, for example, the FCI `make_rdm12s` docstring. This notation has the advantage that when $k = j$ the center becomes a density operator.

Using $\{c_i^\dagger, c_j\} = 0$, it differs by a sign and `swapaxes` from the physics notation (TODO verify this...it's been a while and this is from memory):

$$\rho_{ijkl}^{\uparrow\downarrow} = \langle c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger c_{k\uparrow} c_{l\downarrow}\rangle \tag{9}$$