Spin contamination

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Aug 2022

1 Operators

We define the spin angular momentum of a particle as a vector operator $\vec{s}$:

$$\vec{s} = \begin{pmatrix} \hat{s}_x \\ \hat{s}_y \\ \hat{s}_z \end{pmatrix}$$

and $\hat{s}^2$ as the scalar operator:

$$s^2 = \vec{s} \cdot \vec{s} = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2$$

The components of the spin angular momentum vector satisfy the commutation relations:

$$[\hat{s}_x, \hat{s}_y] = i\hat{s}_z$$

$$[\hat{s}_y, \hat{s}_z] = i\hat{s}_x$$

$$[\hat{s}_z, \hat{s}_x] = i\hat{s}_y$$

Because these operators do not commute (cannot be measured simultaneously), the complete spin state of a particle can be described by the simultaneous eigenfunctions of s^2 and a component of $\vec{s}$, usually $\hat{s}_z$. Therefore, define a spin vector to be of the following form:

$$|s, m_s\rangle$$

where s, m_s are quantum numbers describing total spin and the z component of the spin, defined by their respective operators' action on the wave function:

$$s^2 |s, m_s\rangle = s(s+1) |s, m_s\rangle$$

$$\hat{s}_z |s, m_s\rangle = m_s |s, m_s\rangle$$

$|\alpha\rangle, |\beta\rangle$ are spin basis vectors defined as:

$$|\alpha\rangle \equiv |\tfrac{1}{2}, \tfrac{1}{2}\rangle$$

$$|\beta\rangle \equiv |\tfrac{1}{2}, -\tfrac{1}{2}\rangle$$

We can then show how each operator acts on $|\alpha\rangle, |\beta\rangle$

$\hat{s}_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle$

$\hat{s}_z |\beta\rangle = -\frac{1}{2} |\beta\rangle$

$\hat{s}_x |\alpha\rangle = \frac{1}{2} |\beta\rangle$

$\hat{s}_x |\beta\rangle = \frac{1}{2} |\alpha\rangle$

$\hat{s}_y |\alpha\rangle = \frac{i}{2} |\beta\rangle$

$\hat{s}_y |\beta\rangle = -\frac{i}{2} |\alpha\rangle$

Note that while $|\alpha\rangle, |\beta\rangle$ are eigenfunctions of $s^2, \hat{s}_z$, they are not eigenfunctions of $\hat{s}_x, \hat{s}_y$

Can also define step up and down operators:

$\hat{S}_+ \equiv \hat{s}_x + i\hat{s}_y$

$\hat{S}_- \equiv \hat{s}_x - i\hat{s}_y$

which respectively increase or decrease the value of m_s by 1. We can show the action of $\hat{S}_+, \hat{S}_-$ on the basis vectors $|\alpha\rangle, |\beta\rangle$

$$\begin{aligned}
\hat{S}_+ |\alpha\rangle &= (\hat{s}_x + i\hat{s}_y) |\alpha\rangle && (1)\\
&= \hat{s}_x |\alpha\rangle + i\hat{s}_y |\alpha\rangle && (2)\\
&= \frac{1}{2} |\beta\rangle + \frac{i^2}{2} |\beta\rangle && (3)\\
&= \frac{1}{2} |\beta\rangle - \frac{1}{2} |\beta\rangle && (4)\\
&= 0 && (5)
\end{aligned}$$

$$\begin{aligned}
\hat{S}_+ |\beta\rangle &= (\hat{s}_x + i\hat{s}_y) |\beta\rangle && (6)\\
&= \hat{s}_x |\beta\rangle - i\hat{s}_y |\beta\rangle && (7)\\
&= \frac{1}{2} |\alpha\rangle + \frac{1}{2} |\alpha\rangle && (8)\\
&= |\alpha\rangle && (9)
\end{aligned}$$

$$\begin{aligned}
\hat{S}_- |\alpha\rangle &= (\hat{s}_x - i\hat{s}_y) |\alpha\rangle && (10)\\
&= \hat{s}_x |\alpha\rangle + i\hat{s}_y |\alpha\rangle && (11)\\
&= \frac{1}{2} |\beta\rangle + \frac{1}{2} |\beta\rangle && (12)\\
&= |\beta\rangle && (13)
\end{aligned}$$

$$\hat{S}_- |\beta\rangle = \hat{s}_x |\beta\rangle - i\hat{s}_y |\beta\rangle \tag{14}$$
$$= \frac{1}{2} |\alpha\rangle - \frac{1}{2} |\alpha\rangle \tag{15}$$
$$= 0 \tag{16}$$

We can use the step up/down operators to rewrite s^2:

$$s^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2 \tag{17}$$
$$= (\hat{s}_x + i\hat{s}_y)(\hat{s}_x - i\hat{s}_y) + i\hat{s}_x\hat{s}_y - i\hat{s}_y\hat{s}_x + \hat{s}_z^2 \tag{18}$$
$$= \hat{S}_+\hat{S}_- + i(\hat{s}_x\hat{s}_y - \hat{s}_y\hat{s}_x) + \hat{s}_z^2 \tag{19}$$
$$= \hat{S}_+\hat{S}_- + i[\hat{s}_x, \hat{s}_y] + \hat{s}_z^2 \tag{20}$$
$$= \hat{S}_+\hat{S}_- + i^2\hat{s}_z + \hat{s}_z^2 \tag{21}$$
$$= \hat{S}_+\hat{S}_- - \hat{s}_z + \hat{s}_z^2 \tag{22}$$

and also

$$s^2 = \hat{S}_-\hat{S}_+ + \hat{s}_z + \hat{s}_z^2 \tag{23}$$

Finally, we can define analogous multi-electron versions of all of the above operators.

$\vec{\mathcal{L}} = \sum_i^N \vec{s}(i)$

$\mathcal{L}_\mu \equiv \sum_i^N \hat{S}_\mu(i)$

for $\mu \in \{x, y, z\}$

$\mathcal{L}_\pm = \sum_i^N \hat{S}_\pm(i)$

$$\mathcal{L}^2 = \vec{\mathcal{L}} \cdot \vec{\mathcal{L}} \tag{24}$$
$$= \sum_i^N \sum_j^N \vec{s}(i) \cdot \vec{s}(j) \tag{25}$$
$$= \mathcal{L}_+\mathcal{L}_- - \mathcal{L}_z + \mathcal{L}_z^2 \tag{26}$$
$$= \mathcal{L}_-\mathcal{L}_+ + \mathcal{L}_z + \mathcal{L}_z^2 \tag{27}$$

Where each sum runs over all electrons in the system.

2 Basis sets

In general, a basis set of 2K spin functions can be built in two distinct ways. In the restricted formalism, there is a set of K spatial functions, which are each multiplied by an α or a β to create 2K spin functions:

$$\{\chi_1, \chi_2, ..., \chi_{2K-1}, \chi_{2K}\} = \{\psi_1, \bar{\psi}_1, ..., \psi_K, \bar{\psi}_K\} \quad (28)$$
$$= \{\psi_1\alpha, \psi_1\beta, ..., \psi_K\alpha, \psi_K\beta\} \quad (29)$$

Note that this basis set is orthonormal if the set of spatial functions $\{\psi_1, ..., \psi_K\}$ is orthonormal due to α, β being orthogonal.

In the unrestricted formalism, the $2i$ and $2i-1$ spin basis functions are not constrained to have the same spatial component. Ie.

$$\{\chi_1, \chi_2, ..., \chi_{2K-1}, \chi_{2K}\} = \{\psi_1^\alpha, \bar{\psi}_1^\beta, ..., \psi_K^\alpha, \bar{\psi}_K^\beta\} \quad (30)$$
$$= \{\psi_1^\alpha\alpha, \psi_1^\beta\beta, ..., \psi_K^\alpha\alpha, \psi_K^\beta\beta\} \quad (31)$$

Where

$B^\alpha = \{\psi_1^\alpha, ..., \psi_K^\alpha\}$

$B^\beta = \{\psi_1^\beta, ..., \psi_K^\beta\}$

both form orthonormal basis sets. ψ_i^α and ψ_j^β need not be orthogonal for the overall basis set to be orthonormal (again due to $\langle\alpha|\beta\rangle = 0$). We define the components of the spin overlap matrix $S^{\alpha\beta}$ as

$S_{ij}^{\alpha\beta} = \langle\psi_i^\alpha|\psi_j^\beta\rangle$

From this, we can see that the restricted approximation is a special case where $S^{\alpha\beta}$ is the identity matrix. Ie.

$\langle\psi_i^\alpha|\psi_j^\beta\rangle = \delta_{ij}$

and thus

$\psi_i^\alpha = \psi_i^\beta = \psi_i$

Finally, we note the constraints on the matrix $S^{\alpha\beta}$. We first assume that $\{\psi_i^\alpha\}$ and $\{\psi_i^\beta\}$ span the same space. Ie:

$Sp(\{\psi_i^\alpha\}) = Sp(\{\psi_i^\alpha\} \cup \{\psi_i^\beta\}) = Sp(\{\psi_i^\beta\})$

where Sp is the span. In that case, in combination with the fact that both $\{\psi_i^\alpha\}$ and $\{\psi_i^\beta\}$ are orthonormal, we can expand any function ψ_i^α as a unique linear combination of ψ_j^β. It is trivial to show that the coefficients of this expansion are the elements of the i^{th} row of $S^{\alpha\beta}$:

$$|\psi_i^\alpha\rangle = \sum_j^K |\psi_j^\beta\rangle \langle\psi_j^\beta|\psi_i^\alpha\rangle \tag{32}$$

$$= \sum_j^K S_{ij}^{\alpha\beta *} |\psi_j^\beta\rangle \tag{33}$$

$$= \sum_j^K S_{ij}^{\alpha\beta} |\psi_j^\beta\rangle \tag{34}$$

Using this equality,

$$1 = \langle\psi_i^\alpha|\psi_i^\alpha\rangle = \sum_j^K S_{ij}^{\alpha\beta} \langle\psi_j^\beta| \sum_l^K S_{il}^{\alpha\beta} |\psi_l^\beta\rangle \tag{35}$$

$$= \sum_j^K \sum_l^K S_{ij}^{\alpha\beta} S_{il}^{\alpha\beta} \langle\psi_j^\beta|\psi_l^\beta\rangle \tag{36}$$

$$= \sum_j^K \sum_l^K S_{ij}^{\alpha\beta} S_{il}^{\alpha\beta} \delta_{jl} \tag{37}$$

$$= \sum_j^K S_{ij}^{\alpha\beta} S_{ij}^{\alpha\beta} \tag{38}$$

$$= \sum_j^K S_{ij}^{\alpha\beta\,2} \tag{39}$$

Ie. the sum of the squared elements of any row in $S^{\alpha\beta}$ is exactly equal to 1. Without loss of generality, this can also be proven for each column (by taking the transpose of $S^{\alpha\beta}$), and noting that spatial wave functions are real).

3 Derivations

3.1 $\mathcal{L}_z$

First, we prove that for any single determinant $|\Psi\rangle$,

$$\mathcal{L}_z |\Psi\rangle = \frac{N^\alpha - N^\beta}{2} |\Psi\rangle \tag{40}$$

Ie. any single determinant is an eigenfunction of $\mathcal{L}_z$ with eigenvalue of $\frac{N^\alpha - N^\beta}{2}$, where N^α is the number of occupied α orbitals and β is the number of occupied β orbitals.Using second quantization,

$$\mathcal{L}_z |\Psi\rangle = \sum_p^{2K} \sum_q^{2K} \langle\chi_p| \hat{s}_z |\chi_q\rangle a_p^\dagger a_q |\Psi\rangle \tag{41}$$

$$= \sum_p^{2K} \sum_q^{2K} \langle\psi_p^{\eta_p} \eta_p| \hat{s}_z |\psi_q^{\eta_q} \eta_q\rangle a_p^\dagger a_q |\Psi\rangle \tag{42}$$

$$= \sum_p^{2K} \sum_q^{2K} \langle\psi_p^{\eta_p} |\psi_q^{\eta_q}\rangle \langle\eta_p| \hat{s}_z |\eta_q\rangle a_p^\dagger a_q |\Psi\rangle \tag{43}$$

$$= \frac{1}{2}[\sum_p^{2K} \sum_q^{K_\alpha} \langle\psi_p^{\eta_p}|\psi_q^\alpha\rangle \langle\eta_p|\alpha\rangle a_p^\dagger a_q - \sum_p^{2K} \sum_q^{K_\beta} \langle\psi_p^{\eta_p}|\psi_q^\beta\rangle \langle\eta_p|\beta\rangle a_p^\dagger a_q] |\Psi\rangle \tag{44}$$

$$= \frac{1}{2}[\sum_p^{2K} \sum_q^{K_\alpha} \langle\psi_p^{\eta_p}|\psi_q^\alpha\rangle \delta_{\eta_p \alpha} a_p^\dagger a_q - \sum_p^{2K} \sum_q^{K_\beta} \langle\psi_p^{\eta_p}|\psi_q^\beta\rangle \delta_{\eta_p \beta} a_p^\dagger a_q] |\Psi\rangle \tag{45}$$

$$= \frac{1}{2}[\sum_p^{K_\alpha} \sum_q^{K_\alpha} \langle\psi_p^\alpha|\psi_q^\alpha\rangle a_p^\dagger a_q - \sum_p^{K_\beta} \sum_q^{K_\beta} \langle\psi_p^\beta|\psi_q^\beta\rangle a_p^\dagger a_q] |\Psi\rangle \tag{46}$$

$$= \frac{1}{2}[\sum_p^{K_\alpha} \sum_q^{K_\alpha} \delta_{pq} a_p^\dagger a_q - \sum_p^{K_\beta} \sum_q^{K_\beta} \delta_{pq} a_p^\dagger a_q] |\Psi\rangle \tag{47}$$

$$= \frac{1}{2}[\sum_p^{K_\alpha} a_p^\dagger a_p - \sum_p^{K_\beta} a_p^\dagger a_p] |\Psi\rangle \tag{48}$$

$$\tag{49}$$

Here, we note that the terms with a a_p operator annihilating a virtual orbital will vanish:

$$= \frac{1}{2}[\sum_i^{N_\alpha} a_i^\dagger a_i - \sum_i^{N_\beta} a_i^\dagger a_i] |\Psi\rangle \tag{50}$$

$$= \frac{1}{2}[\sum_i^{N_\alpha}(\delta_{ii} - a_i a_i^\dagger) - \sum_i^{N_\beta}(\delta_{ii} - a_i a_i^\dagger)] |\Psi\rangle \tag{51}$$

$$= \frac{1}{2}[\sum_i^{N_\alpha} \delta_{ii} - \sum_i^{N_\beta} \delta_{ii}] |\Psi\rangle \tag{52}$$

$$= \frac{1}{2}[N_\alpha - N_\beta] |\Psi\rangle \tag{53}$$

$$= \frac{N_\alpha - N_\beta}{2} |\Psi\rangle \tag{54}$$

3.2 Spin contamination

Want to find the expectation value of $\mathcal{L}^2$ for a determinant in general. Ie.

$$\langle \mathcal{L}^2 \rangle_{UHF} = \langle\Psi| \mathcal{L}^2 |\Psi\rangle \tag{55}$$

$$= \langle\Psi| \mathcal{L}_- \mathcal{L}_+ + \mathcal{L}_z + \mathcal{L}_z^2 |\Psi\rangle \tag{56}$$

$$= \langle\Psi| \mathcal{L}_- \mathcal{L}_+ |\Psi\rangle + \langle\Psi| \mathcal{L}_z |\Psi\rangle + \langle\Psi| \mathcal{L}_z^2 |\Psi\rangle \tag{57}$$

Using the result from section 3.1,

$$\langle\Psi| \mathcal{L}_z |\Psi\rangle = \frac{N_\alpha - N_\beta}{2} \tag{58}$$

for a normalized determinant $|\Psi\rangle$. Similarly,

$$\langle\Psi| \mathcal{L}^2 |\Psi\rangle = \frac{N_\alpha - N_\beta}{2} \langle\Psi| \mathcal{L} |\Psi\rangle \tag{59}$$

$$= (\frac{N_\alpha - N_\beta}{2})^2 \tag{60}$$

For the first term, we again use second quantization:

$$\langle\Psi|\,\mathcal{L}_-\mathcal{L}_+\,|\Psi\rangle = \sum_{pqrs}^{2K} \langle\psi_p^{\eta_p}\eta_p|\,\hat{S}_-\,|\psi_q^{\eta_q}\eta_q\rangle\,\langle\psi_r^{\eta_r}\eta_r|\,\hat{S}_+\,|\psi_s^{\eta_s}\eta_s\rangle\,\langle\Psi|\,a_p^\dagger a_q a_r^\dagger a_s\,|\Psi\rangle \tag{61}$$

$$= \sum_{pqrs}^{2K} \langle\psi_p^{\eta_p}|\psi_q^{\eta_q}\rangle\,\langle\eta_p|\,\hat{S}_-\,|\eta_q\rangle\,\langle\psi_r^{\eta_r}|\psi_s^{\eta_s}\rangle\,\langle\eta_r|\,\hat{S}_+\,|\eta_s\rangle\,\langle\Psi|\,a_p^\dagger a_q a_r^\dagger a_s\,|\Psi\rangle \tag{62}$$

Terms with $\eta_q = \beta$ and $\eta_s = \alpha$ vanish due to the step down/up operators

$$= \sum_{pr}^{2K}\sum_{q}^{K_\alpha}\sum_{s}^{K_\beta} \langle\psi_p^{\eta_p}|\psi_q^{\alpha}\rangle\,\langle\eta_p|\,\hat{S}_-\,|\alpha\rangle\,\langle\psi_r^{\eta_r}|\psi_s^{\beta}\rangle\,\langle\eta_r|\,\hat{S}_+\,|\beta\rangle\,\langle\Psi|\,a_p^\dagger a_q a_r^\dagger a_s\,|\Psi\rangle \tag{63}$$

$$= \sum_{pr}^{2K}\sum_{q}^{K_\alpha}\sum_{s}^{K_\beta} \langle\psi_p^{\eta_p}|\psi_q^{\alpha}\rangle\,\langle\eta_p|\beta\rangle\,\langle\psi_r^{\eta_r}|\psi_s^{\beta}\rangle\,\langle\eta_r|\alpha\rangle\,\langle\Psi|\,a_p^\dagger a_q a_r^\dagger a_s\,|\Psi\rangle \tag{64}$$

$\eta_p = \alpha, \eta_q = \beta$ vanish.

$$= \sum_{ps}^{K_\beta}\sum_{qr}^{K_\alpha} \langle\psi_p^{\beta}|\psi_q^{\alpha}\rangle\,\langle\psi_r^{\alpha}|\psi_s^{\beta}\rangle\,\langle\Psi|\,a_p^\dagger a_q a_r^\dagger a_s\,|\Psi\rangle \tag{65}$$

$$= \sum_{ps}^{K_\beta}\sum_{qr}^{K_\alpha} S_{qp}^{\alpha\beta\,*} S_{rs}^{\alpha\beta}\,\langle\Psi|\,a_p^\dagger a_q a_r^\dagger a_s\,|\Psi\rangle \tag{66}$$

Terms with p, s indices over virtual orbitals vanish

$$= \sum_{ij}^{N_\beta}\sum_{qr}^{K_\alpha} S_{qi}^{\alpha\beta\,*} S_{rj}^{\alpha\beta}\,\langle\Psi|\,a_i^\dagger a_q a_r^\dagger a_j\,|\Psi\rangle \tag{67}$$

$$= \sum_{ij}^{N_\beta}\sum_{qr}^{K_\alpha} S_{qi}^{\alpha\beta\,*} S_{rj}^{\alpha\beta}\,\langle\Psi|\,(\delta_{iq} - a_q a_i^\dagger)(\delta_{rj} - a_j a_r^\dagger)\,|\Psi\rangle \tag{68}$$

$$= \sum_{ij}^{N_\beta}\sum_{qr}^{K_\alpha} S_{qi}^{\alpha\beta\,*} S_{rj}^{\alpha\beta}\,\langle\Psi|\,a_q a_i^\dagger a_j a_r^\dagger\,|\Psi\rangle \tag{69}$$

Terms with q, r indices over occupied orbitals vanish

$$= \sum_{ij}^{N_\beta} \sum_{ab}^{K_\alpha - N_\alpha} S_{ai}^{\alpha\beta *} S_{bj}^{\alpha\beta} \langle\Psi| a_a a_i^\dagger a_j a_b^\dagger |\Psi\rangle \tag{70}$$

Here, one can get an intuition about what $\mathcal{L}_\pm$ does. For $\mathcal{L}_+$ on the right, there is an excitation from each occupied β orbital j to each virtual α orbital a, multiplied by the overlap between the spatial components of j and a. Using Wick's theorem:

$$= \sum_{ij}^{N_\beta} \sum_{ab}^{K_\alpha - N_\alpha} S_{ai}^{\alpha\beta *} S_{bj}^{\alpha\beta} \langle\Psi| a_j a_a^\dagger a_b a_i^\dagger - \delta_{ba} a_j a_i^\dagger - \delta_{ij} a_a^\dagger a_b + \delta_{ba}\delta_{ij} |\Psi\rangle \tag{71}$$

$$= \sum_{ij}^{N_\beta} \sum_{ab}^{K_\alpha - N_\alpha} S_{ai}^{\alpha\beta *} S_{bj}^{\alpha\beta} \delta_{ab}\delta ij \langle\Psi| |\Psi\rangle \tag{72}$$

$$= \sum_{i}^{N_\beta} \sum_{a}^{K_\alpha - N_\alpha} S_{ai}^{\alpha\beta *} S_{ai}^{\alpha\beta} \tag{73}$$

$$= \sum_{i}^{N_\beta} \sum_{a}^{K_\alpha - N_\alpha} |S_{ai}^{\alpha\beta}|^2 \tag{74}$$

Using the constraint derived in section 2,

$$1 = \sum_{i}^{K - N_\alpha} |S_{ij}^{\alpha\beta}|^2 + \sum_{i}^{N_\alpha} |S_{ij}^{\alpha\beta}|^2 \tag{75}$$

$$\tag{76}$$

Then

$$\sum_{i}^{K_\alpha - N_\alpha} |S_{ij}^{\alpha\beta}|^2 = 1 - \sum_{i}^{N_\alpha} |S_{ij}^{\alpha\beta}|^2 \tag{77}$$

and

$$\sum_{j}^{N_\beta}\sum_{a}^{K_\alpha - N_\alpha} |S_{ai}^{\alpha\beta}|^2 = \sum_{j}^{N_\beta}(1 - \sum_{i}^{N_\alpha} |S_{ij}^{\alpha\beta}|^2) \tag{78}$$

$$= N_\beta - \sum_{i}^{N_\alpha}\sum_{j}^{N_\beta} |S_{ij}^{\alpha\beta}|^2 \tag{79}$$

Finally, putting it all together,

$$\langle\Psi| \mathcal{L}^2 |\Psi\rangle = (\frac{N_\alpha - N_\beta}{2})^2 + \frac{N_\alpha - N_\beta}{2} + N_\beta - \sum_{i}^{N_\alpha}\sum_{j}^{N_\beta} |S_{ij}^{\alpha\beta}|^2 \tag{80}$$

$$= (\frac{N_\alpha - N_\beta}{2} + 1)\frac{N_\alpha - N_\beta}{2} + N_\beta - \sum_{i}^{N_\alpha}\sum_{j}^{N_\beta} |S_{ij}^{\alpha\beta}|^2 \tag{81}$$

For the case of RHF, we can see that Eq. 81 reduces to

$$(\frac{N_\alpha - N_\beta}{2} + 1)\frac{N_\alpha - N_\beta}{2} + N_\beta - \sum_{i}^{N_\alpha}\sum_{j}^{N_\beta} \delta_{ij}^2 \tag{82}$$

$$= (\frac{N_\alpha - N_\beta}{2} + 1)\frac{N_\alpha - N_\beta}{2} + N_\beta - \sum_{i}^{N_\alpha}\sum_{j}^{N_\beta} 1 \tag{83}$$

$$= (\frac{N_\alpha - N_\beta}{2} + 1)\frac{N_\alpha - N_\beta}{2} + N_\beta - \sum_{j}^{N_\beta} 1 \tag{84}$$

$$= (\frac{N_\alpha - N_\beta}{2} + 1)\frac{N_\alpha - N_\beta}{2} + N_\beta - N_\beta \tag{85}$$

$$= (\frac{N_\alpha - N_\beta}{2} + 1)\frac{N_\alpha - N_\beta}{2} \equiv \langle\mathcal{L}^2\rangle_{RHF} \tag{86}$$

At which point we arrive at the equation given in Szabo and Ostlund [1]:

$$\langle\Psi| \mathcal{L}^2 |\Psi\rangle = \langle\mathcal{L}^2\rangle_{RHF} + N_\beta - \sum_{i}^{N_\alpha}\sum_{j}^{N_\beta} |S_{ij}^{\alpha\beta}|^2 \tag{87}$$

References

[1] Attila Szabo and Neil S. Ostlund. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Dover Publications, 1996.