# Independent Study Assignment: Week 10

Daniel J. Staros

November 7, 2019

## 1 Szabo: Modern Quantum Chemistry

### 1.14. Show that $a(0) = \int_{-\infty}^{\infty} a(x)\delta(x)dx$.

The delta function was defined according to equations 1 and 2.

$$a(x') = \int a(x) \left[ \sum_i \psi_i(x)\psi_i^*(x') \right] dx \tag{1}$$

$$\sum_i \psi_i(x)\psi_i^*(x') = \delta(x - x') \tag{2}$$

Evaluating $a(0)$ in accordance with these definitions, it is obtained that

$$a(0) = \int a(x) \left[ \sum_i \psi_i(x)\psi_i^*(0) \right] dx = \int a(x)\delta(x-0)(x)dx = \int a(x)\delta(x)dx,$$

which was to be shown.

### 1.16. Show that $\mathcal{O}\phi(x) = \omega\phi(x)$ is equivalent to $\mathbf{Oc} = \omega\mathbf{c}$.

Expanding $\phi$ in terms of the complete set $\psi_i$, $\mathcal{O}\phi(x) = \omega\phi(x)$ becomes

$$\mathcal{O}\sum_{i=1}^{\infty} c_i\psi_i = \omega\sum_{i=1}^{\infty} c_i\psi_i \to \sum_{i=1}^{\infty} c_i\left(\mathcal{O}\psi_i\right) = \omega\sum_{i=1}^{\infty} c_i\left(\psi_i\right)$$

which, upon multiplication by $\psi_j^*$ and integration yields

$$\sum_{i=1}^{\infty} c_i\left(\int \psi_j^*\mathcal{O}\psi_i\right) = \omega\sum_{i=1}^{\infty} c_i\left(\int \psi_j^*\psi_i\right).$$

Since $\mathbf{O}_{ij} = \int \psi_j^*\mathcal{O}\psi_i$ and $\int \psi_j^*\psi_i = \delta_{ij}$, the above expression becomes

$$\sum_{i=1}^{\infty} \mathbf{O}_{ij}c_i = \omega\sum_{i=1}^{\infty} c_i\delta_{ij} \to \sum_{i=1}^{\infty} \mathbf{O}_{ij}c_i = \omega c_j \to \mathbf{Oc} = \omega\mathbf{c}.$$

## 1.17. Demonstrate Dirac notation as instructed.

### a.

Multiplying $\int |x\rangle \langle x| \, dx$ on the left with $\langle i|$ and right with $|j\rangle$ and noting that $\langle i|x\rangle = \psi_i^*(x)$ and $\langle x|j\rangle = \psi_J(x)$, we have

$$\int |x\rangle \langle x| \, dx = 1 \rightarrow \int \langle i|x\rangle \langle x|j\rangle \, dx = \int \psi_i^*(x)\psi_j(x)dx = \delta_{ij},$$

which is the same as equation 1.116:

$$\int_{x_1}^{x_2} dx \; \psi_i^*(x)\psi_j(x) = \delta_{ij}. \tag{1.116}$$

### b.

Multiplying $\sum_{i=1}^{\infty} |i\rangle \langle i|$ on the left with $\langle x|$ and right with $|x'\rangle$ and noting that $\langle x|x'\rangle = \delta(x - x')$, we have

$$\sum_{i=1}^{\infty} \langle x|i\rangle \langle i|x'\rangle \left( = \sum_{i=1}^{\infty} \psi_i^*(x)\psi_j(x') \right) = \langle x| \left( \cancelto{1}{\sum_{i=1}^{\infty} |i\rangle \langle i|} \right) |x'\rangle = \langle x|x'\rangle = \delta(x - x').$$

Evidently, this is the same as equation 1.120:

$$\sum_{i=1}^{\infty} \psi_i^*(x)\psi_j(x') = \delta(x - x'). \tag{1.120}$$

### c.

Multiplying $\int |x\rangle \langle x| \, dx$ on the left with $\langle x'|$ and right with $|a\rangle$, we have

$$\int |x\rangle \langle x| \, dx = 1 \rightarrow \int \langle x'|x\rangle \langle x|a\rangle \, dx = \int \delta(x' - x)a(x)dx$$

since $\langle x'|x\rangle = \delta(x' - x)$ and $\langle x|a\rangle = a(x)$. This is the same as equation 1.121:

$$a(x) = \int \delta(x' - x)a(x)dx. \tag{1.121}$$

### d.

Starting with $|b\rangle = \int dx \, \mathcal{O} \, |x\rangle \langle x|a\rangle$,

$$\langle x'|b\rangle = \int dx \; \langle x'| \, \mathcal{O} \, |x\rangle \langle x|a\rangle = \int dx \, O(x', x)a(x)$$

again using $\langle x|a\rangle = a(x)$. This result is the same as equation 1.133.

**e.**

From $O(x,x') = \langle x|O|x'\rangle$ and $O_{ij} = \langle i|O|j\rangle$,

$$O(x,x') = \langle x|O|x'\rangle = \langle x|i\rangle \langle i|O|j\rangle \langle j|x'\rangle = \int \psi_i^*(x) O_{ij} \psi_j(x') dx.$$

## Demonstrate that $e^{A+B} \neq e^A e^B$ if A and B do not commute. What is the Baker-Haussdorff-Campbell rule and how does it relate to these exponentials? What about Suzuki-Trotter factorization?

For some $e^X$, the Baker-Hausdorff-Campbell rule states that an equivalent expression is $I + X + \frac{X^2}{2!} + [...]$ . Thus, for $e^A e^B$,

$$e^A e^B = (I + A + \frac{A^2}{2!} + ...)(I + B + \frac{B^2}{2!} + ...) \tag{1}$$

$$= I + A + B + AB + \frac{AB^2}{2!} + \frac{A^2}{2!} + \frac{BA^2}{2!} + \frac{B^2}{2!} + ... \tag{2}$$

which may be rewritten as

$$= I + A + B + \frac{A^2 + 2AB + B^2}{2!} + \frac{A^3}{3!} + \frac{AB^2}{2!} + \frac{BA^2}{2!} + \frac{B^3}{3!} + [...] . \tag{3}$$

But, when A and B commute, $A^2 + 2AB + B^2 = (A + B)^2$ and the above may be rewritten as the expansion of $e^{(A+B)}$,

$$e^{(A+B)} = I + A + B + \frac{(A + B)^2}{2!} + \frac{(A + B)^3}{3!} + [...] .$$

Thus, if A and B do not commute, the jump from expression 3 to this simplified expression is not possible, and $e^{(A+B)} \neq e^A e^B$.

Suzuki-Trotter expansion is a way to generalize the expression of exponential operators. The first order expansion may be written: $e^{(A+B)} = \lim_{n\to\infty} \left(e^{\frac{A}{n}} e^{\frac{B}{n}}\right)^n$. Although Suzuki-Trotter factorization was not directly used in this problem, it might be used to more develop more general description than above why $e^{A+B} \neq e^A e^B$ if A and B do not commute.

# Independent Study Assignment: Week 11

Daniel J. Staros

November 15, 2019

## Szabo: Modern Quantum Chemistry

**2.2. Show that $\Psi_{HP}(x_1, x_2, x_3, ..., x_n) = \chi_i(x_1)\chi_j(x_2), ..., \chi_k(x_3)$ is an eigenfunction of $H = \sum_i^N h(i)$ with an eigenvalue $E = \epsilon_i + \epsilon_j + ... + \epsilon_k$.**

From the above,

$$H\Psi_{HP} = \sum_i^N h(i)(\chi_i(x_1)\chi_j(x_2), ..., \chi_k(x_3))$$

which becomes

$$H\Psi_{HP} = h(1)\chi_i(x_1) + h(2)\chi_j(x_2)+, ..., +h(3)\chi_k(x_3)$$

since $h(i)$ only acts on the $i^{th}$ electron. The above, using equation 2.29, is the sum of eigenfunction equations equal to $h(1)\epsilon_i + h(2)\epsilon_j+, ..., +h(3)\epsilon_k$. Thus, the corresponding sum of eigenvalues is $E = \epsilon_i + \epsilon_j + ... + \epsilon_k$, which was to be shown.

**2.4. Show that $\Psi_{12}^{HP}$, $\Psi_{21}^{HP}$ and $\Psi$ are eigenfunctions of $H = h(1) + h(2)$ with eigenvalue $E = \epsilon_i + \epsilon_j$.**

Keeping in mind that $h(i)\chi_j(x_i) = \epsilon_i\chi_j(x_i)$ and that $h(i)$ only operates on $\chi_i$,

$$H\Psi_{12}^{HP} = (h(1) + h(2))\chi_i(x_1)\chi_j(x_2) = (h(1)\chi_i(x_1))\chi_j(x_2) + \chi_i(x_1)(h(2)\chi_j(x_2))$$

$$= (\epsilon_i\chi_i(x_1))\chi_j(x_2) + \chi_i(x_1)(\epsilon_j\chi_j(x_2)) = \epsilon_i(\chi_i(x_1)\chi_j(x_2)) + \epsilon_j(\chi_i(x_1)\chi_j(x_2)).$$

Thus,

$$H\Psi_{12}^{HP} = (\epsilon_i + \epsilon_j)\chi_i(x_1)\chi_j(x_2) = E\Psi_{12}^{HP}$$

Using the same procedure on $\Psi_{21}^{HP}$ yields that $\mathrm{H}\Psi_{21}^{HP} = (\epsilon_i + \epsilon_j)\chi_i(x_2)\chi_j(x_1) = E\Psi_{21}^{HP}$. Keeping these two relations in mind, one can write $\mathrm{H}\Psi(x_1, x_2)$ as follows,

$$H\left(\frac{1}{\sqrt{2}}(\Psi_{12}^{HP} + \Psi_{21}^{HP})\right) = \frac{1}{\sqrt{2}}\left[(h(1)+h(2))\Psi_{12}^{HP} + (h(1)+h(2))\Psi_{21}^{HP}\right]$$

$$= \frac{1}{\sqrt{2}}(\epsilon_i + \epsilon_j)\left(\Psi_{12}^{HP} + \Psi_{21}^{HP}\right) = (\epsilon_i + \epsilon_j)\left(\frac{1}{\sqrt{2}}(\Psi_{12}^{HP} + \Psi_{21}^{HP})\right) = E\Psi(x_1, x_2)$$

## 2.5. Where $|K\rangle = |\chi_i\chi_j\rangle$ and $|L\rangle = |\chi_k\chi_l\rangle$, show that $\langle K|L\rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$.

The following expressions are true by definition,

$$\langle K| = \begin{vmatrix} \chi_i(1)^* & \chi_i(2)^* \\ \chi_j(1)^* & \chi_j(2)^* \end{vmatrix};\ |L\rangle = \begin{vmatrix} \chi_k(1) & \chi_l(1) \\ \chi_k(2) & \chi_l(2) \end{vmatrix}.$$

From this,

$$\langle K|L\rangle = \frac{1}{2}\left(\begin{vmatrix} \chi_i(1)^* & \chi_i(2)^* \\ \chi_j(1)^* & \chi_j(2)^* \end{vmatrix}\right)\left(\begin{vmatrix} \chi_k(1) & \chi_l(1) \\ \chi_k(2) & \chi_l(2) \end{vmatrix}\right)$$

$$= \frac{1}{2}\left(\chi_i(1)^*\chi_j(2)^* - \chi_i(2)^*\chi_j(1)^*\right)\left(\chi_k(1)\chi_l(2) - \chi_l(1)\chi_k(2)\right)$$

$$= \frac{1}{2}\chi_i(1)^*\chi_k(1)\chi_j(2)^*\chi_l(2) - \chi_i(1)^*\chi_l(1)\chi_j(2)^*\chi_k(2)$$
$$-\chi_i(2)^*\chi_l(2)\chi_j(1)^*\chi_k(1) + \chi_i(2)^*\chi_k(2)\chi_j(1)^*\chi_l(1)$$

Integration of which over the entire range yields

$$= \frac{1}{2}\left(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} - \delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl}\right) = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}.$$

# Independent Study Assignment: Week 12

Daniel J. Staros

November 22, 2019

## Szabo: Modern Quantum Chemistry - Chp. 2.3

### 2.7. For minimal basis benzene described by 72 spin orbitals, what is the size of the full CI matrix? How many singly and doubly excited determinants are there?

In this case, benzene has $N = 30$ electrons and $2K = 72$ spin orbitals which yields $\binom{2K}{N} = \binom{72}{30} = \frac{72!}{30!(42!)} = 1.64 * 10^{20}$ determinants in the full CI matrix. Since each electron can be excited twice, either with spin up or spin down, the number of singly excited determinants is $2 * (1.64 * 10^{20}) = 3.28 * 10^{20}$ singly excited determinants. Similarly, the number of pairs of electrons, chosen two at a time to be excited is $\binom{30}{2} = \frac{30!}{2!(28!)} = 435$ ways to doubly excite the system excluding consideration of spin. Since each pair of electrons can be excited with 4 different spin combinations, there are 1,740 ways to doubly excite the system. Thus, the number of doubly excited determinants is $1,740 * (1.64 * 10^{20}) = 2.85 * 10^{24}$.

### 2.8. Show that $\langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_{12}^{34} \rangle = \langle 3|h|3\rangle + \langle 4|h|4\rangle$ and $\langle \Psi_0 | \mathcal{O}_1 | \Psi_{12}^{34} \rangle = \langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_0 \rangle = 0$.

By definition, $|\Psi_{12}^{34}\rangle = |\chi_3\chi_4\rangle$ and $\langle \Psi_{12}^{34}| = \langle \chi_3\chi_4|$. It is given that $\mathcal{O}_1 = h(1) + h(2)$. We then have

$$\langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_{12}^{34} \rangle = \langle \Psi_{12}^{34} | h(1) | \Psi_{12}^{34} \rangle + \langle \Psi_{12}^{34} | h(2) | \Psi_{12}^{34} \rangle$$

Note that the notation $|\chi_i\chi_j\rangle$ is shorthand for the determinant

$$\begin{vmatrix} \chi_i(1) & \chi_i(2) \\ \chi_j(1) & \chi_j(2) \end{vmatrix}$$

From this, the spin-orbital integral representation of the $h(1)$ term is

$$\int dx_1 dx_2 \left[(2^{-1/2})\chi_3(x_1)\chi_4(x_2) - \chi_3(x_2)\chi_4(x_1)\right]^* h(\mathbf{r}_1) \left[(2^{-1/2})\chi_3(x_1)\chi_4(x_2) - \chi_3(x_2)\chi_4(x_1)\right]$$

which expands to

$$\frac{1}{2}\int dx_1 dx_2 [\chi_3(x_1)^*\chi_4(x_2)^* h(\mathbf{r}_1)\chi_3(x_1)\chi_4(x_2) - \cancelto{0}{\chi_3(x_1)^*\chi_4(x_2)^* h(\mathbf{r}_1)\chi_3(x_2)\chi_4(x_1)} -$$

$$\cancelto{0}{\chi_3(x_2)^*\chi_4(x_1)^* h(\mathbf{r}_1)\chi_3(x_1)\chi_4(x_2)} + \chi_3(x_2)^*\chi_4(x_1)^* h(\mathbf{r}_1)\chi_3(x_2)\chi_4(x_1)]$$

where the second and third terms become zero due to the orthogonality of the spin orbitals. Integrating over electron 1, the above becomes

$$\frac{1}{2}\int dx_1 \chi_3(x_1)^* h(\mathbf{r}_1)\chi_3(x_1) + \frac{1}{2}\int dx_1 \chi_4(x_1)^* h(\mathbf{r}_1)\chi_4(x_1).$$

The same treatment for $h(2)$ yields the same result, and the above 1/2 coefficients become 1, leaving

$$\langle \Psi_{12}^{34}|\mathcal{O}_1|\Psi_{12}^{34}\rangle = \langle \Psi_{12}^{34}|h(1)+h(2)|\Psi_{12}^{34}\rangle =$$

$$\int dx_1 \chi_3(x_1)^* h(\mathbf{r}_1)\chi_3(x_1) + \int dx_1 \chi_4(x_1)^* h(\mathbf{r}_1)\chi_4(x_1) = \langle 3|h|3\rangle + \langle 4|h|4\rangle$$

where the last equality was obtained using the notation provided in Szabo. Thus, the first equality in the question has been verified. The second equality need not be evaluated explicitly, as all spin-orbital components of $|\Psi_0\rangle$ are orthogonal to all spin-orbital components of $|\Psi_{12}^{34}\rangle$, which will inevitably yield that $\langle \Psi_0|\mathcal{O}_1|\Psi_{12}^{34}\rangle = \langle \Psi_{12}^{34}|\mathcal{O}_1|\Psi_0\rangle = 0$.

## 2.9. Show the full CI matrix for minimal basis $H_2$, and demonstrate that it is Hermitian.

The CI matrix for $H_2$ consists of a linear combination of the ground state and doubly excited state as written in the matrix below:

$$\begin{pmatrix} \langle \Psi_0|\mathcal{H}|\Psi_0\rangle & \langle \Psi_0|\mathcal{H}|\Psi_{12}^{34}\rangle \\ \langle \Psi_{12}^{34}|\mathcal{H}|\Psi_0\rangle & \langle \Psi_{12}^{34}|\mathcal{H}|\Psi_{12}^{34}\rangle \end{pmatrix} = \begin{pmatrix} \langle \Psi_0|\mathcal{O}_1+\mathcal{O}_2|\Psi_0\rangle & \langle \Psi_0|\mathcal{O}_1+\mathcal{O}_2|\Psi_{12}^{34}\rangle \\ \langle \Psi_{12}^{34}|\mathcal{O}_1+\mathcal{O}_2|\Psi_0\rangle & \langle \Psi_{12}^{34}|\mathcal{O}_1+\mathcal{O}_2|\Psi_{12}^{34}\rangle \end{pmatrix}$$

Note that the first component of $\langle \Psi_{12}^{34}|\mathcal{O}_1+\mathcal{O}_2|\Psi_{12}^{34}\rangle$ was calculated in the previous exercise. The second component requires evaluation of $\langle \Psi_{12}^{34}|r_{12}|\Psi_{12}^{34}\rangle$, which is below.

$$\frac{1}{2}\int dx_1 dx_2 [\chi_3(x_1)^*\chi_4(x_2)^* r_{12}\chi_3(x_1)\chi_4(x_2) - \chi_3(x_1)^*\chi_4(x_2)^* r_{12}\chi_3(x_2)\chi_4(x_1) -$$

$$\chi_3(x_2)^*\chi_4(x_1)^* r_{12}\chi_3(x_1)\chi_4(x_2) + \chi_3(x_2)^*\chi_4(x_1)^* r_{12}\chi_3(x_2)\chi_4(x_1)]$$

Since $r_{12} = r_{12}$, one can reverse the 1/2 designations in the third and fourth terms, making them equal to the second and first terms respectively. The above then becomes

$$\int dx_1 dx_2 \chi_3(x_1)^* \chi_4(x_2)^* r_{12} \chi_3(x_1)\chi_4(x_2) - \int dx_1 dx_2 \chi_3(x_1)^* \chi_4(x_2)^* r_{12} \chi_3(x_2)\chi_4(x_1).$$

The above may be written $\langle 34|34\rangle - \langle 34|43\rangle$ using the notation of Szabo. We now know that $\langle \Psi_{12}^{34}|\mathcal{H}|\Psi_{12}^{34}\rangle = \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34|34\rangle - \langle 34|43\rangle$. It was shown in Szabo that, similarly, $\langle \Psi_0|\mathcal{H}|\Psi_0\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle$. Further, reasoning in the previous problem concluded that $\langle \Psi_0|\mathcal{O}_1|\Psi_{12}^{34}\rangle = \langle \Psi_{12}^{34}|\mathcal{O}_1|\Psi_0\rangle = 0$. However, $\langle \Psi_0|\mathcal{O}_2|\Psi_{12}^{34}\rangle$ will not equal 0 since two electron integrals are required. Consultation of the result obtained in this problem supports the conclusion that $\langle \Psi_0|\mathcal{O}_2|\Psi_{12}^{34}\rangle$ will equal $\langle 12|34\rangle - \langle 12|43\rangle$ and $\langle \Psi_{12}^{34}|\mathcal{O}_2|\Psi_0\rangle$ will equal $\langle 34|12\rangle - \langle 34|21\rangle$. Putting all of these results into the initial CI matrix definition of this exercise, the minimal basis CI matrix for $H_2$ is:

$$\begin{pmatrix} \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle & \langle 12|34\rangle - \langle 12|43\rangle \\ \langle 34|12\rangle - \langle 34|21\rangle & \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34|34\rangle - \langle 34|43\rangle \end{pmatrix}$$

which was to be shown. The adjoint of this matrix is

$$\begin{pmatrix} [\langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle]^* & [\langle 34|12\rangle - \langle 34|21\rangle]^* \\ [\langle 12|34\rangle - \langle 12|43\rangle]^* & [\langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34|34\rangle - \langle 34|43\rangle]^* \end{pmatrix}$$

which, switching the bra and ket terms of all the entries (or applying the conjugation) yields

$$\begin{pmatrix} \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle & \langle 12|34\rangle - \langle 12|43\rangle \\ \langle 34|12\rangle - \langle 34|21\rangle & \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34|34\rangle - \langle 34|43\rangle \end{pmatrix}$$

which is the same as the original matrix. Thus, this matrix is Hermitian.

## 2.10. Derive Eqn. 2.110 from 2.107.

$$\langle K|\mathcal{H}|K\rangle = \langle K|\mathcal{O}_1 + \mathcal{O}_2|K\rangle = \sum_m^N \langle m|h|m\rangle + \frac{1}{2}\sum_m^N \sum_n^N \langle mn||mn\rangle \qquad (2.107)$$

$$\langle K|\mathcal{H}|K\rangle = \sum_m [m|h|m] + \sum_m^N \sum_{n>m}^V [mm|nn] - [mn|nm] \qquad (2.110)$$

Starting with the integral form of Eqn 2.107, we have

$$\langle K|\mathcal{H}|K\rangle = \sum_m^N \left(\int dx_1 \chi_m(x_1)^* h(r_1)\chi_m(x_1)\right) + \frac{1}{2}\sum_m^N\sum_n^N [\int dx_1 dx_2 \chi_m(x_1)^*\chi_n(x_2)^* r_{12}^{-1}\chi_m(x_1)\chi_n(x_2) -$$

$$\int dx_1 dx_2 \chi_m(x_1)^*\chi_n(x_2)^* r_{12}^{-1}\chi_n(x_1)\chi_m(x_2)].$$

which, using the chemist's notation for the first summation and rearranging the terms within the integrals of the second summation,

$$= \sum_m^N [m|h|m] + \frac{1}{2}\sum_m^N\sum_n^N [\int dx_1 dx_2 \chi_m(x_1)^*\chi_m(x_1) r_{12}^{-1}\chi_n(x_2)^*\chi_n(x_2) -$$

$$\int dx_1 dx_2 \chi_m(x_1)^*\chi_n(x_2)^* r_{12}^{-1}\chi_n(x_1)\chi_m(x_2)].$$

Using the chemists notation for the second part, the whole equation becomes

$$\langle K|\mathcal{H}|K\rangle = \sum_m [m|h|m] + \sum_m^N \sum_{n>m}^V [mm|nn] - [mn|nm]$$

which was to be shown.

## 2.13. Show that $\langle \Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle = ...$

**a. 0 if** $a \neq b, r \neq s$

When $a \neq b$ and $r \neq s$, $\langle \Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle = \langle \chi_r\chi_b|h|\chi_a\chi_s\rangle = \int dx \chi_r^*\chi_b^* h\chi_a\chi_s = 0$ due to the orthogonality of the spin-orbitals, and the fact that $a \neq b$ and $r \neq s$.

**b.** $\langle r|h|s\rangle$ **if** $a = b, r \neq s$

When $a = b$ and $r \neq s$, $\langle \Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle = \langle \chi_r\chi_b|h|\chi_a\chi_s\rangle = \int dx \chi_r^*\chi_b^* h\chi_a\chi_s = \int dx \chi_r^* h\chi_s = \langle r|h|s\rangle$ since $\langle \chi_b|\chi_a\rangle = 1$ when $a = b$.

**c.** $-\langle b|h|a\rangle$ **if** $a \neq b, r = s$

When $a \neq b$ and $r = s$, $\langle \Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle = \langle \chi_r\chi_b|h|\chi_a\chi_s\rangle = \int dx \chi_r^*\chi_b^* h\chi_a\chi_s = -\int dx \chi_b^*\chi_r^* h\chi_s\chi_a = -\int dx \chi_b^* h\chi_a = -\langle b|h|a\rangle$ since $\langle \chi_r|\chi_s\rangle = 1$ when $r = s$.

**d.** $\sum_c^N \langle c|h|c\rangle - \langle a|h|a\rangle + \langle r|h|r\rangle$ **if** $a = b, r = s$

When $a = b$ and $r = s$, $\langle \Psi_a^r|\mathcal{O}_1|\Psi_b^s\rangle = \langle \chi_r\chi_b\chi_c...|h|\chi_a\chi_s\chi_c...\rangle = \int dx \chi_r^*\chi_b^*\chi_c^*(...)h\chi_a\chi_s\chi_c(...) = \int dx \chi_r^*\chi_a^*\chi_c^*(...)h\chi_a\chi_r\chi_c(...) = -\int dx \chi_r^*\chi_c^*\chi_a^*(...)h\chi_a\chi_r\chi_c(...) = -\int dx \chi_r^*\chi_c^*(...)h\chi_r\chi_c(...) - \langle a|h|a\rangle = \int dx \chi_r^*\chi_c^*(...)h\chi_c\chi_r(...) - \langle a|h|a\rangle = \int dx \chi_r^*(...)h\chi_r(...) + \langle c|h|c\rangle - \langle a|h|a\rangle$ which, continuing up to some $\chi_N$ (denoted by the ellipsis) $= \sum_c^N \langle c|h|c\rangle - \langle a|h|a\rangle + \langle r|h|r\rangle$.

# Independent Study Assignment: Week 13

Daniel J. Staros

December 6, 2019

## Szabo: Modern Quantum Chemistry - Chp. 2.3

### 2.17. Integrate out spin in the full CI matrix for minimal basis $H_2$ and express it below.

The result obtained in 2.9 for the CI matrix of minimal basis $H_2$ was

$$\begin{pmatrix} \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle & \langle 12|34\rangle - \langle 12|43\rangle \\ \langle 34|12\rangle - \langle 34|21\rangle & \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34|34\rangle - \langle 34|43\rangle \end{pmatrix}.$$

From Eqns. 2.60 and 2.65 of Szabo, we know that the (1,1) element of the above matrix may be evaluated as follows:

$$\langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle =$$

$$\int dx_1 \psi_1(\mathbf{r}_1)^* \alpha(\omega_1)^* h(\mathbf{r}_1) \psi_1(\mathbf{r}_1) \alpha(\omega_1) + \int dx_1 \psi_1(\mathbf{r}_1)^* \beta(\omega_1)^* h(\mathbf{r}_1) \psi_1(\mathbf{r}_1) \beta(\omega_1)$$

$$+ \int dx_1 \psi_1(r_1)^* \alpha(\omega_1)^* \psi_1(r_2)^* \beta(\omega_2)^* r_{12}^{-1} \psi_1(r_1) \alpha(\omega_1) \psi_1(r_2) \beta(\omega_2)$$

$$- \int dx_1 \psi_1(r_1)^* \alpha(\omega_1)^* \psi_1(r_2)^* \beta(\omega_2)^* r_{12}^{-1} \psi_1(r_2) \beta(\omega_2) \psi_1(r_1) \alpha(\omega_1)$$

which, since $\langle \alpha|\beta\rangle = 0$ and $\langle \beta|\alpha\rangle = 0$ in the last term, yields

$$= (1|h|1) + (1|h|1) + (11|11) = 2(1|h|1) + (11|11)$$

with the new notation for one-electron spatial integrals. Identically, but with spin orbitals 3 and 4, the (2,2) entry of the initial matrix is evidently $2(2|h|2) + (22|22)$. Now we must determine cross terms.

Without explicitly writing the integrals, one may recognize that entry (1,2) $= \langle 12|34\rangle - \langle 12|43\rangle = (12|12) - 0$ since spin orbitals 1 and 3 both have $\alpha$ components while 2 and 4 both have $\beta$ components. A similar conclusion is drawn about entry (2,1), which correspondingly equals (21|21). Thus, the full CI matrix of minimal basis $H_2$ with spin components integrated out is

$$\begin{pmatrix} 2(1|h|1) + (11|11) & (12|12) \\ (21|21) & 2(2|h|2) + (22|22) \end{pmatrix}.$$

**2.19. Prove the following properties of coulomb and exchange integrals: $J_{ii} = K_{ii}, J^*_{ij} = J_{ij}, K^*_{ij} = K_{ij}, J_{ij} = J_{ji}, K_{ij} = K_{ji}$.**

The definitions of the Coulomb integral and exchange integral are given respectively in equations 1 and 2:

$$J_{ij} = (ii|jj) = \int dr_1 dr_2 |\psi_i(\mathbf{r}_1)|^2 r_{12}^{-1} |\psi_j(\mathbf{r}_2)|^2 \tag{1}$$

$$K_{ij} = (ij|ji) = \int dr_1 dr_2 \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1) r_{12}^{-1} \psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2) \tag{2}$$

From these definitions, $J_{ii} = (ii|ii)$ and $K_{ii} = (ii|ii)$. Evidently, $J_{ii} = K_{ii} = (ii|ii)$. To see this somewhat more thoroughly, consider the integral expression of $K_{ij}$ when j = i. When this is the case, $\psi_i^*\psi_j$ for electrons 1 and 2 become the probability clouds of the Coulomb integral, which by definition are equal to $(ii|ii)$.

Consider now $J^*_{ij}$. Every component within the definition of $J_{ij}$ in Eqn. 1 is real, since probability densities and physical distances cannot be imaginary. Thus, the complex conjugate of this real value is itself, and $J^*_{ij} = J_{ij}$.

The above argument cannot be made exactly for the equivalence of $K^*_{ij}$ and $K_{ij}$. Instead, one can assess the complex conjugate of Eqn. 2,

$$K^*_{ij} = \int dr_1 dr_2 \psi_i(\mathbf{r}_1)\psi_j^*(\mathbf{r}_1) r_{12}^{-1} \psi_j(\mathbf{r}_2)\psi_i^*(\mathbf{r}_2)$$

which, upon exchange of electrons 1 and 2 (since they are identical), yields

$$K^*_{ij} = \int dr_1 dr_2 \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1) r_{12}^{-1} \psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2) = K_{ij},$$

thereby demonstrating what was to be shown.

Explicitly, $J_{ji} = (jj|ii)$. The integral form of this expression is

$$\int dr_1 dr_2 |\psi_j(\mathbf{r}_1)|^2 r_{12}^{-1} |\psi_i(\mathbf{r}_2)|^2$$

which, upon exchange of electrons 1 and 2 yields the expression

$$\int dr_1 dr_2 |\psi_i(\mathbf{r}_1)|^2 r_{12}^{-1} |\psi_j(\mathbf{r}_2)|^2.$$

This expression is equal to Eqn. 1, or $J_{ij}$.

Lastly, consider the expression for $K_{ji}$,

$$K_{ji} = \int dr_1 dr_2 \psi_j^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1) r_{12}^{-1} \psi_i^*(\mathbf{r}_2)\psi_j(\mathbf{r}_2)$$

Another simple exchange of electrons yields that

$$K_{ji} = \int dr_1 dr_2 \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1) r_{12}^{-1} \psi_j^*(\mathbf{r}_2)\psi_i(\mathbf{r}_2) = K_{ij}.$$

## 2.21. Show the full CI matrix for minimal basis $H_2$ given in Szabo is correct.

As given in the response to question 2.17, the full CI matrix for minimal basis $H_2$ is

$$\begin{pmatrix} 2(1|h|1) + (11|11) & (12|12) \\ (21|21) & 2(2|h|2) + (22|22) \end{pmatrix}.$$

By definition, $(ii|ii) = J_{ii}$, $(12|12) = K_{12}$, $(21|21) = K_{12}$ after consideration of the previous exercise, and $(i|h|i) = h_{ii}$. Thus, the above matrix may be written

$$\begin{pmatrix} 2h_{11} + J_{11} & K_{12} \\ K_{12} & 2h_{22} + J_{22} \end{pmatrix}$$

which was to be shown.

## 2.23. Verify the energies of the given determinants by inspection.

**a.** $h_{11} + h_{22} + J_{12} - K_{12}$

The energy of the electron in spatial orbital 1 is $h_{11}$, the energy of the electron in spatial orbital 2 is $h_{22}$, the coulomb repulsion energy of the two electrons is $J_{12}$, and the exchange energy due to the parallel spins of the two electrons is given by $-K_{12}$.

**b.** $h_{11} + h_{22} + J_{12}$

The energy of the electron in spatial orbital 1 is $h_{11}$, the energy of the electron in spatial orbital 2 is $h_{22}$, the coulomb repulsion energy of the two electrons is $J_{12}$, and their is no exchange energy contribution due to the antiparallel spins of the two electrons.

**c.** $2h_{11} + J_{11}$

Since both electrons are in spatial orbital 1, the energy contribution is $2h_{11}$. The coulomb repulsion energy is $J_{11}$ since both electrons are in orbital 1.

**d.** $2h_{22} + J_{22}$

Since both electrons are in spatial orbital 2, the energy contribution is $2h_{22}$. The coulomb repulsion energy is $J_{22}$ since both electrons are in orbital 2.

**e.** $2h_{11} + h_{22} + J_{11} + 2J_{12} - K_{12}$

This energy is the same as the answer to c, but with additional contributions from the spin-up electron in orbital 2. These additional contributions are $h_{22}$ due to the presence of the additional electron, $2J_{12}$ due to the coulomb repulsion of both electrons in orbital 1 with the electron in orbital 2, and $-K_{12}$ due to the exchange energy associated with the parallel spins of the spin-up electrons in orbitals 1 and 2.

**f.** $2h_{22} + h_{11} + J_{22} + 2J_{12} - K_{12}$

The same reasoning employed in the answer to e easily justifies the form of the energy in diagram f.

**g.** $2h_{11} + 2h_{22} + J_{11} + J_{22} + 4J_{12} - 2K_{12}$

Here, $2h_{11}$ corresponds to the presence of two electrons in orbital 1, $2h_{22}$ to the two electrons in orbital 2, $J_{11}$ to the coulomb repulsion of electrons in orbital 1, $J_{22}$ to the coulomb repulsion of electrons in orbital 2, $4J_{12}$ due to the coulomb repulsion between the two electrons each in energy levels 1 and 2, and lastly $-2K_{12}$ due to the exchange energy resulting from of parallel spins between spin-up and spin-down electrons in energy level 1 and 2.

# Independent Study: Final Assignment

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## Szabo: Modern Quantum Chemistry - Chp. 2.4

### 2.25. Show the appropriate relations using properties of determinants.

Consider the set $|K\rangle : \{|\chi_1\chi_2\rangle, |\chi_1\chi_3\rangle, |\chi_1\chi_4\rangle, |\chi_2\chi_3\rangle, |\chi_2\chi_4\rangle, |\chi_3\chi_4\rangle\}$. In the case

$$(a_1 a_2^\dagger + a_2^\dagger a_1)|K\rangle = a_1 a_2^\dagger |K\rangle + a_2^\dagger a_1 |K\rangle$$

The definitions of creation and annihilation operators turn the set $|K\rangle$ into

$$(a_1 a_2^\dagger |\chi_1\chi_2\rangle + a_2^\dagger a_1 |\chi_1\chi_2\rangle), (a_1 a_2^\dagger |\chi_1\chi_3\rangle + a_2^\dagger a_1 |\chi_1\chi_3\rangle), (a_1 a_2^\dagger |\chi_1\chi_4\rangle + a_2^\dagger a_1 |\chi_1\chi_4\rangle),$$

$$(\cancelto{0}{a_1 a_2^\dagger |\chi_2\chi_3\rangle} + \cancelto{0}{a_2^\dagger a_1 |\chi_2\chi_3\rangle}), (\cancelto{0}{a_1 a_2^\dagger |\chi_2\chi_4\rangle} + \cancelto{0}{a_2^\dagger a_1 |\chi_2\chi_4\rangle}), (a_1 a_2^\dagger |\chi_3\chi_4\rangle + \cancelto{0}{a_2^\dagger a_1 |\chi_3\chi_4\rangle})$$

since creation operators acting on spin orbitals that already exist yield 0, as do annihilation operators acting on spin orbitals that do not exist. This expression is equal to

$$(-a_1 \cancelto{0}{a_2^\dagger |\chi_2\chi_1\rangle} + \cancelto{0}{a_2^\dagger |\chi_2\rangle}), (-a_1 |\chi_1\chi_2\chi_3\rangle + |\chi_2\chi_3\rangle), (-a_1 |\chi_1\chi_2\chi_4\rangle + |\chi_2\chi_4\rangle), 0, 0, \cancelto{0}{a_1 |\chi_2\chi_3\chi_4\rangle}$$

where some spin orbital positions were switched and signs changed accordingly. This is now equal to

$$0, \cancelto{0}{(-|\chi_2\chi_3\rangle + |\chi_2\chi_3\rangle)}, \cancelto{0}{(-|\chi_2\chi_4\rangle + |\chi_2\chi_4\rangle)}, 0, 0, 0 = \{0, 0, 0, 0, 0, 0\}.$$

### 2.26. Show using second quantization that $\langle\chi_i|\chi_j\rangle = \delta_{ij}$.

The components $\langle\chi_i|$ and $|\chi_j\rangle$ may be written respectively as operators acting on the vacuum state: $\langle| a_i$ and $a_j^\dagger |\rangle$. Then, $\langle\chi_i|\chi_j\rangle$ becomes $\langle|a_i a_j^\dagger|\rangle = \langle|\delta_{ij} - a_i^\dagger a_j|\rangle$ which becomes $\langle|\delta_{ij}|\rangle - \cancelto{0}{\langle|a_i^\dagger a_j\rangle|} = \delta_{ij}\langle||\rangle = \delta_{ij}$ since the annihilation operator acting on the vacuum state is equal to 0.

**2.27. Given a state $|K\rangle = |\chi_1\chi_2...\chi_N\rangle = a_1^\dagger a_2^\dagger ... a_N^\dagger\, |\rangle$, show that $\langle K|a_i^\dagger a_j|K\rangle = 1$ if $i = j$ and $i \in 1, 2, ..., N$, but is zero otherwise.**

By definition, we have that $\langle K| = \langle|\, a_N ... a_2 a_1$ and $|K\rangle = a_1^\dagger a_2^\dagger ... a_N^\dagger\, |\rangle$. Thus,

$$\langle K|a_i^\dagger a_j|K\rangle = \langle|\, a_N ... a_2 a_1 a_i^\dagger a_j a_1^\dagger a_2^\dagger ... a_N^\dagger\, |\rangle = -\langle|\, a_N ... a_2 a_1 (1 - a_i a_i^\dagger) a_1^\dagger a_2^\dagger ... a_N^\dagger\, |\rangle$$

when $i = j$, which is equivalent to the expression

$$\langle|\, a_N ... a_2 a_1 (1) a_1^\dagger a_2^\dagger ... a_N^\dagger\, |\rangle - \langle|\, a_N ... a_2 a_1 \cancelto{0}{a_i a_i^\dagger} a_1^\dagger a_2^\dagger ... a_N^\dagger\, |\rangle = \langle \chi_N ... \chi_2\chi_1|\chi_1\chi_2...\chi_N\rangle - 0$$

$$= 1 - 0 = 1.$$

In the case that $i \in 1, 2, ..., N$, one could switch positions on spin orbitals in the second term above such that $a_i$ and $a_i^\dagger$ were still next to one another, making the expression 0. This is what was to be shown.

**2.29. For the Hartree Fock wave function $|\Psi(0)\rangle = |\chi_1\chi_2\rangle = a_1^\dagger a_2^\dagger\, |\rangle$, use second quantization to show the desired relationship.**

$$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle = \langle|\, a_2 a_1 \left(\sum_{i,j} \langle i|h|j\rangle\, a_i^\dagger a_j\right) a_1^\dagger a_2^\dagger\, |\rangle = \langle|\, a_2 a_1 \left(\sum_{1,2} \langle 1|h|2\rangle\, a_1^\dagger a_2\right) a_1^\dagger a_2^\dagger\, |\rangle$$

$$= \langle|\, a_2 a_1 \left(\langle 1|h|1\rangle + \langle 1|h|2\rangle + \langle 2|h|1\rangle + \langle 2|h|2\rangle\right) a_1^\dagger a_2 a_1^\dagger a_2^\dagger\, |\rangle$$

$$= \langle 1|h|1\rangle \langle|a_2 a_1 (1 - a_1 a_1^\dagger) a_1^\dagger a_2^\dagger|\rangle + \langle 1|h|2\rangle \cancelto{0}{\langle|a_2 a_1 (a_1^\dagger a_2) a_1^\dagger a_2^\dagger|\rangle}$$

$$+ \langle 2|h|1\rangle \cancelto{0}{\langle|a_2 a_1 (a_2^\dagger a_1) a_1^\dagger a_2^\dagger|\rangle} + \langle 2|h|2\rangle \langle|a_2 a_1 (1 - a_2 a_2^\dagger) a_1^\dagger a_2^\dagger|\rangle$$

$$= \langle 1|h|1\rangle \left(\langle\chi_2\chi_1|(1)|\chi_1\chi_2\rangle - \cancelto{0}{\langle\chi_2\chi_1|(a_1 a_1^\dagger)|\chi_1\chi_2\rangle}\right)$$

$$+ \langle 2|h|2\rangle \left(\langle\chi_2\chi_1|(1)|\chi_1\chi_2\rangle - \cancelto{0}{\langle\chi_2\chi_1|(a_2 a_2^\dagger)|\chi_1\chi_2\rangle}\right)$$

$$= \langle 1|h|1\rangle \cancelto{1}{\langle\chi_2\chi_1|\chi_1\chi_2\rangle} + \langle 2|h|2\rangle \cancelto{1}{\langle\chi_2\chi_1|\chi_1\chi_2\rangle} = \langle 1|h|1\rangle + \langle 2|h|2\rangle\,.$$

**2.31. Show that $\langle \Psi_a^r | \mathcal{O}_2 | \Psi_0 \rangle = \sum_b^N \langle rb || ab \rangle$ using 2.27.**

First, consider the expression $\langle \Psi_0 | a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k | \Psi_0 \rangle$ where $|\Psi_0\rangle \equiv |\chi_1 ... \chi_a \chi_b ... \chi_N\rangle$. Manipulating this,

$$\langle \Psi_0 | a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k | \Psi_0 \rangle = \delta_{ri} \langle \Psi_0 | a_a^\dagger a_j^\dagger a_l a_k | \Psi_0 \rangle - \langle \Psi_0 | a_i^\dagger a_r a_j^\dagger a_l a_k | \Psi_0 \rangle$$

$$= -\delta_{ri}\delta_{al} \langle \Psi_0 | a_j^\dagger a_k | \Psi_0 \rangle + \delta_{ri} \langle \Psi_0 | a_j^\dagger a_l a_a^\dagger a_k | \Psi_0 \rangle - \langle \Psi_0 | a_i^\dagger a_r a_j^\dagger a_l a_k | \Psi_0 \rangle$$

$$= -\delta_{ri}\delta_{al} \langle \Psi_0 | a_j^\dagger a_k | \Psi_0 \rangle + \delta_{ri}\delta_{ak} \langle \Psi_0 | a_j^\dagger a_l | \Psi_0 \rangle + \delta_{ri} \cancelto{0}{\langle \Psi_0 | a_a^\dagger a_l a_k a_j^\dagger | \Psi_0 \rangle} - \langle \Psi_0 | a_i^\dagger a_r a_j^\dagger a_l a_k | \Psi_0 \rangle$$

where the third term above is zero since one cannot create a $j$ spin orbital where there already is one. Continuing, the above is equal to

$$-\delta_{ri}\delta_{al} \langle \Psi_0 | a_j^\dagger a_k | \Psi_0 \rangle + \delta_{ri}\delta_{ak} \langle \Psi_0 | a_j^\dagger a_l | \Psi_0 \rangle + \delta_{rj} \langle \Psi_0 | a_i^\dagger a_a^\dagger a_l a_k | \Psi_0 \rangle + \cancelto{0}{\langle \Psi_0 | a_i^\dagger a_a^\dagger a_j^\dagger a_k a_l a_r | \Psi_0 \rangle}$$

since $a_r |\Psi_0\rangle$ is attempting to annihilate a spin orbital which does not exist in $|\Psi_0\rangle$. From here, we have

$$= -\delta_{ri}\delta_{al} \langle \Psi_0 | a_j^\dagger a_k | \Psi_0 \rangle + \delta_{ri}\delta_{ak} \langle \Psi_0 | a_j^\dagger a_l | \Psi_0 \rangle + \delta_{rj}\delta_{al} \langle \Psi_0 | a_i^\dagger a_k | \Psi_0 \rangle - \delta_{rj} \langle \Psi_0 | a_i^\dagger a_l a_a^\dagger a_k | \Psi_0 \rangle$$

$$= -\delta_{ri}\delta_{al} \langle \Psi_0 | a_j^\dagger a_k | \Psi_0 \rangle + \delta_{ri}\delta_{ak} \langle \Psi_0 | a_j^\dagger a_l | \Psi_0 \rangle + \delta_{rj}\delta_{al} \langle \Psi_0 | a_i^\dagger a_k | \Psi_0 \rangle - \delta_{rj}\delta_{ak} \langle \Psi_0 | a_i^\dagger a_l | \Psi_0 \rangle$$
$$- \cancelto{0}{\langle \Psi_0 | a_a^\dagger a_l a_k a_i^\dagger | \Psi_0 \rangle}$$

where again, an $i$ spin orbital cannot be created where there already is one. Thus, we have shown that

$$\langle \Psi_0 | a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k | \Psi_0 \rangle = \delta_{rj}\delta_{al} \langle \Psi_0 | a_i^\dagger a_k | \Psi_0 \rangle - \delta_{rj}\delta_{ak} \langle \Psi_0 | a_i^\dagger a_l | \Psi_0 \rangle + \delta_{ri}\delta_{ak} \langle \Psi_0 | a_j^\dagger a_l | \Psi_0 \rangle$$
$$- \delta_{ri}\delta_{al} \langle \Psi_0 | a_j^\dagger a_k | \Psi_0 \rangle .$$

One can use this result to evaluate $\langle \Psi_a^r | \mathcal{O}_2 | \Psi_0 \rangle$. By definition of $\mathcal{O}_2$ and the fact that $\langle \Psi_a^r | = \langle \Psi_0 | a_a^\dagger a_r$,

$$\langle \Psi_a^r | \mathcal{O}_2 | \Psi_0 \rangle = \langle \Psi_a^r | \left( \frac{1}{2} \sum_{ijkl} \langle ij|kl \rangle a_i^\dagger a_j^\dagger a_l a_k \right) | \Psi_0 \rangle = \frac{1}{2} \sum_{ijkl} \langle \Psi_0 | a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k | \Psi_0 \rangle \langle ij|kl \rangle$$

Notice that we have already obtained an expression for $\langle \Psi_0 | a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k | \Psi_0 \rangle$, which we can substitute to yield that $\langle \Psi_a^r | \mathcal{O}_2 | \Psi_0 \rangle$ is equal to

$$\frac{1}{2} \sum_{ijkl} \Big( \delta_{rj}\delta_{al} \langle \Psi_0 | a_i^\dagger a_k | \Psi_0 \rangle - \delta_{rj}\delta_{ak} \langle \Psi_0 | a_i^\dagger a_l | \Psi_0 \rangle + \delta_{ri}\delta_{ak} \langle \Psi_0 | a_j^\dagger a_l | \Psi_0 \rangle - \delta_{ri}\delta_{al} \langle \Psi_0 | a_j^\dagger a_k | \Psi_0 \rangle \Big) \langle ij|kl \rangle$$

$$= \frac{1}{2}\sum_{ijkl}(\delta_{rj}\delta_{al}\langle\Psi_0|a_i^\dagger a_k|\Psi_0\rangle\langle ij|kl\rangle + \delta_{ri}\delta_{ak}\langle\Psi_0|a_j^\dagger a_l|\Psi_0\rangle\langle ij|kl\rangle$$

$$-\delta_{rj}\delta_{ak}\langle\Psi_0|a_i^\dagger a_l|\Psi_0\rangle\langle ij|kl\rangle - \delta_{ri}\delta_{al}\langle\Psi_0|a_j^\dagger a_k|\Psi_0\rangle\langle ij|kl\rangle).$$

Accounting for delta function equalities, this is equivalent to

$$\frac{1}{2}\sum_b^N 2\langle rb|ab\rangle - 2\langle rb|ba\rangle = \sum_b^N \langle rb|ab\rangle - \langle rb|ba\rangle = \sum_b^N \langle rb||ab\rangle$$

where the sum is up to $N$ due to the requirement from exercise 2.27 that $\langle K|a_i^\dagger a_j|K\rangle = 1$ if $i = j$ and $i \in 1, 2, ..., N$.