Appendix A: Derivation of the real-space representation of the effective interaction projected in a basis set

The exact Coulomb electron-electron operator can be expressed in real-space second quantization as

$$\hat{W}_{\text{ee}} = \frac{1}{2} \iiiint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \, \text{d}\mathbf{X}_3 \, \text{d}\mathbf{X}_4 \, \delta(\mathbf{X}_1 - \mathbf{X}_4) \; \delta(\mathbf{X}_2 - \mathbf{X}_3) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 \,|} \hat{\Psi}^\dagger(\mathbf{X}_4) \, \hat{\Psi}^\dagger(\mathbf{X}_3) \, \hat{\Psi}(\mathbf{X}_2) \, \hat{\Psi}(\mathbf{X}_1) \,, \tag{A1}$$

where $\hat{\Psi}(\mathbf{X})$ and $\hat{\Psi}^\dagger(\mathbf{X})$ are annihilation and creation field operators, and $\mathbf{X} = (\mathbf{r}, \sigma)$ collects the space and spin variables. The Coulomb electron-electron operator restricted to a basis set $\mathcal{B}$ can be written in orbital-space second quantization:

$$\hat{W}_{\text{ee}}^{\mathcal{B}} = \frac{1}{2} \sum_{ijkl \, \in \, \mathcal{B}} V_{ij}^{kl} \; \hat{a}_k^\dagger \hat{a}_l^\dagger \hat{a}_j \hat{a}_i, \tag{A2}$$

where the summations run over all (real-valued) orthonormal spin-orbitals $\{\phi_i(\mathbf{X})\}$ in the basis set $\mathcal{B}$, V_{ij}^{kl} are the two-electron integrals, the annihilation and creation operators can be written in terms of the field operators as

$$\hat{a}_i = \int \text{d}\mathbf{X} \; \phi_i(\mathbf{X}) \; \hat{\Psi}(\mathbf{X}) \,, \tag{A3}$$

$$\hat{a}_i^\dagger = \int \text{d}\mathbf{X} \; \phi_i(\mathbf{X}) \; \hat{\Psi}^\dagger(\mathbf{X}) \,. \tag{A4}$$

Therefore, by defining

$$w^{\mathcal{B}}(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \mathbf{X}_4) = \sum_{ijkl \, \in \, \mathcal{B}} V_{ij}^{kl} \; \phi_k(\mathbf{X}_4) \phi_l(\mathbf{X}_3) \phi_j(\mathbf{X}_2) \phi_i(\mathbf{X}_1) \,, \tag{A5}$$

we can rewrite $\hat{W}_{\text{ee}}^{\mathcal{B}}$ in real-space second quantization as

$$\hat{W}_{\text{ee}}^{\mathcal{B}} = \frac{1}{2} \iiiint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \, \text{d}\mathbf{X}_3 \, \text{d}\mathbf{X}_4 \, w^{\mathcal{B}}(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \mathbf{X}_4) \, \hat{\Psi}^\dagger(\mathbf{X}_4) \, \hat{\Psi}^\dagger(\mathbf{X}_3) \, \hat{\Psi}(\mathbf{X}_2) \, \hat{\Psi}(\mathbf{X}_1) \,. \tag{A6}$$

In the limit of a complete basis set (written as "$\mathcal{B} \to \infty$"), $\hat{W}_{\text{ee}}^{\mathcal{B}}$ coincides with $\hat{W}_{\text{ee}}$:

$$\lim_{\mathcal{B} \to \infty} \hat{W}_{\text{ee}}^{\mathcal{B}} = \hat{W}_{\text{ee}}, \tag{A7}$$

which implies that

$$\lim_{\mathcal{B} \to \infty} w^{\mathcal{B}}(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \mathbf{X}_4) = \delta(\mathbf{X}_1 - \mathbf{X}_4) \; \delta(\mathbf{X}_2 - \mathbf{X}_3) \; \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{A8}$$

It is important here to stress that the definition $w^{\mathcal{B}}(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \mathbf{X}_4)$ tends to a distribution in the limit of a complete basis set, and therefore such an object must really be considered as a distribution acting on test functions and not as a function to be evaluated pointwise. This is why we need to use an expectation value in order to make sense out of $w^{\mathcal{B}}(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \mathbf{X}_4)$.

From equation (A1), the expectation value of the Coulomb electron-electron operator over a wave function Ψ is, after integration over $\mathbf{X}_3$ and $\mathbf{X}_4$,

$$\langle \Psi | \hat{W}_{\text{ee}} | \Psi \rangle = \frac{1}{2} \iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \; \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \langle \Psi | \hat{\Psi}^\dagger(\mathbf{X}_1) \, \hat{\Psi}^\dagger(\mathbf{X}_2) \, \hat{\Psi}(\mathbf{X}_2) \, \hat{\Psi}(\mathbf{X}_1) | \Psi \rangle, \tag{A9}$$

which, by introducing the two-body density matrix,

$$n_{\Psi}^{(2)}(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \mathbf{X}_4) = \langle \Psi | \hat{\Psi}^\dagger(\mathbf{X}_4) \, \hat{\Psi}^\dagger(\mathbf{X}_3) \, \hat{\Psi}(\mathbf{X}_2) \, \hat{\Psi}(\mathbf{X}_1) | \Psi \rangle, \tag{A10}$$

turns into

$$\langle \Psi | \hat{W}_{\text{ee}} | \Psi \rangle = \frac{1}{2} \iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \; \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 \,|} \; n_{\Psi}^{(2)}(\mathbf{X}_1, \mathbf{X}_2), \tag{A11}$$

where $n_{\Psi}^{(2)}(\mathbf{X}_1, \mathbf{X}_2) = n_{\Psi}^{(2)}(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_2, \mathbf{X}_1)$ is the pair density of Ψ. Equation (A11) holds for any wave function Ψ. Consider now the expectation value of $\hat{W}_{\text{ee}}^{\mathcal{B}}$ over a wave function $\Psi^{\mathcal{B}}$. From equation (A6), we get

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}}^{\mathcal{B}} | \Psi^{\mathcal{B}} \rangle = \frac{1}{2} \iiiint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \, \text{d}\mathbf{X}_3 \, \text{d}\mathbf{X}_4 \, w^{\mathcal{B}}(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \mathbf{X}_4) n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \mathbf{X}_4), \tag{A12}$$

where $n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \mathbf{X}_4)$ is expressed as

$$n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \mathbf{X}_4) = \sum_{mnpq \, \in \, \mathcal{B}} \phi_p(\mathbf{X}_4) \phi_q(\mathbf{X}_3) \phi_n(\mathbf{X}_2) \phi_m(\mathbf{X}_1) \; \Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}], \tag{A13}$$

and $\Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}]$ is the two-body density tensor of $\Psi^{\mathcal{B}}$

$$\Gamma_{mn}^{pq}[\Psi^{\mathcal{B}}] = \langle \Psi^{\mathcal{B}} | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_n \hat{a}_m | \Psi^{\mathcal{B}} \rangle. \tag{A14}$$

By integrating over $\mathbf{X}_3$ and $\mathbf{X}_4$ in equation (A12), it comes:

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}}^{\mathcal{B}} | \Psi^{\mathcal{B}} \rangle = \frac{1}{2} \iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \; f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2), \tag{A15}$$

where we introduced the function

$$f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) = \sum_{ijklmn \, \in \, \mathcal{B}} V_{ij}^{kl} \; \Gamma_{kl}^{mn}[\Psi^{\mathcal{B}}] \; \phi_n(\mathbf{X}_2) \phi_m(\mathbf{X}_1) \phi_i(\mathbf{X}_1) \phi_j(\mathbf{X}_2). \tag{A16}$$

From the definition of the restriction of an operator to the space generated by the basis set $\mathcal{B}$, we have the following equality

$$\langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}}^{\mathcal{B}} | \Psi^{\mathcal{B}} \rangle = \langle \Psi^{\mathcal{B}} | \hat{W}_{\text{ee}} | \Psi^{\mathcal{B}} \rangle, \tag{A17}$$

which translates into

$$\begin{aligned} &\frac{1}{2} \iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \; f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) \\ = &\frac{1}{2} \iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \; \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 \,|} \; n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{X}_1, \mathbf{X}_2), \end{aligned} \tag{A18}$$

and holds for any $\Psi^{\mathcal{B}}$. Therefore, by introducing the following function

$$W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) = \frac{f_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2)}{n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{X}_1, \mathbf{X}_2)}, \tag{A19}$$

one can rewrite equation (A18) as

$$\begin{aligned} &\iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \; W_{\Psi^{\mathcal{B}}}(\mathbf{X}_1, \mathbf{X}_2) \; n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{X}_1, \mathbf{X}_2) \\ = &\iint \text{d}\mathbf{X}_1 \, \text{d}\mathbf{X}_2 \; \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 \,|} \; n_{\Psi^{\mathcal{B}}}^{(2)}(\mathbf{X}_1, \mathbf{X}_2). \end{aligned} \tag{A20}$$