Relating orbital and parameter equations

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CONTENTS

I. NOTATION

The Hamiltonian is written using physicist's notation for the integrals (which are not anti-symmetrized):

$$H = \sum_{pq} h_{pq} c_p^\dagger \tilde{c}_q + \frac{1}{2} \sum_{pqrs} u_{pqrs} c_p^\dagger c_q^\dagger \tilde{c}_s \tilde{c}_r \tag{1}$$

$$h_{pq} = \langle \tilde{\varphi}_p | h | \varphi_q \rangle \equiv \int \tilde{\varphi}_p(\mathbf{x}) h(\mathbf{x}) \varphi_q(\mathbf{x}) \, \mathrm{d}\mathbf{x} \tag{2}$$

$$u_{pqrs} = \langle \tilde{\varphi}_p \tilde{\varphi}_q | u | \varphi_r \varphi_s \rangle \equiv \iint \tilde{\varphi}_p(\mathbf{x}) \tilde{\varphi}_q(\mathbf{y}) u(\mathbf{x}, \mathbf{y}) \varphi_r(\mathbf{x}) \varphi_s(\mathbf{y}) \, \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{y} \tag{3}$$

Density matrices are defined as

$$\rho_{qp} = \langle \tilde{\Psi} | c_p^\dagger \tilde{c}_q | \Psi \rangle, \tag{4}$$

$$\rho_{rspq} = \langle \tilde{\Psi} | c_p^\dagger c_q^\dagger \tilde{c}_s \tilde{c}_r | \Psi \rangle. \tag{5}$$

The two-electron integrals and densities have the following useful permutation symmetries:

$$u_{pqrs} = u_{qpsr}, \tag{6}$$

$$\rho_{rspq} = \rho_{srqp}. \tag{7}$$

II. CONVERTING ORBITAL EQUATIONS TO PARAMETER EQUATIONS

The orbital equations are formally identical for all orbital-adaptive methods. Following Kvaal[1] and Sato[2], they take the appearance

$$i \, |\dot{\varphi}_p\rangle = i \sum_q |\varphi_q\rangle \, \eta_{qp} + Q \Big[h \, |\varphi_p\rangle + \sum_{oqrs} W_{rs} \, |\varphi_q\rangle \, P_{qsor} \, (\mathbf{D}^{-1})_{op} \Big], \tag{8}$$

$$i \, \langle \dot{\tilde{\varphi}}_p| = -i \sum_q \eta_{pq} \, \langle \tilde{\varphi}_q| - \Big[\langle \tilde{\varphi}_p| \, h + \sum_{oqrs} (\mathbf{D}^{-1})_{po} \, P_{osqr} \, \langle \tilde{\varphi}_q| \, W_{rs} \Big] Q. \tag{9}$$

The mean-field operator[3,4] W_{rs} is a multiplicative/local operator given by

$$W_{rs}(\mathbf{x}) = \int \tilde{\varphi}_r(\mathbf{y}) u(\mathbf{x}, \mathbf{y}) \varphi_s(\mathbf{y}) \, \mathrm{d}\mathbf{y} \, . \tag{10}$$

Kvaal[1] uses a slightly different notation, but the meaning should be the same. The secondary-space projector is given by

$$Q = 1 - \sum_p |\varphi_p\rangle\langle\tilde{\varphi}_p| \,. \tag{11}$$

The definitions of the densities depend on whether biorthogonal[1] or orthogonal[4] orbitals are used. In the biorthogonal case, the plain one- and two-electron densities are used:

$$D_{qp} = \rho_{qp}, \tag{12}$$

$$P_{rspq} = \rho_{rspq}. \tag{13}$$

In the orthogonal case, the densities are Hermitianized according to

$$D_{qp} = \tfrac{1}{2}(\rho_{qp} + \rho^*_{pq}), \tag{14}$$

$$P_{rspq} = \tfrac{1}{2}(\rho_{rspq} + \rho^*_{pqrs}). \tag{15}$$

Having on orthogonal basis of course means $\langle\tilde{\varphi}_p| = \langle\varphi_p|$, which implies $Q = Q^\dagger$ and $W^*_{rs} = W_{sr}$. Using these relations and the Hermitianized densities one easily confirms that Eqs. (8) and (9) are simply each other's adjoint, when the orbitals are orthogonal.

We now introduce an underlying/primitive basis that is assumed to be biorthonormal. The time-dependent orbitals are given in terms of this basis as

$$|\varphi_p\rangle = \sum_\alpha |\chi_\alpha\rangle\, C_{\alpha p}, \tag{16}$$

$$\langle\tilde{\varphi}_p| = \sum_\alpha \tilde{C}_{p\alpha}\, \langle\tilde{\chi}_\alpha| \,, \tag{17}$$

with time-dependent coefficients. The primitive basis induces the following identity in the one-particle space:

$$1 = \sum_\beta |\chi_\beta\rangle\langle\tilde{\chi}_\beta| \tag{18}$$

Inserting this identity into Eq. (8) and projecting onto $\langle\tilde{\chi}_\alpha|$ yields

$$i\,\langle\tilde{\chi}_\alpha|\dot{\varphi}_p\rangle = i\sum_q \langle\tilde{\chi}_\alpha|\varphi_q\rangle\, \eta_{qp} + \sum_\beta \langle\tilde{\chi}_\alpha|Q|\chi_\beta\rangle \Big[\langle\tilde{\chi}_\beta|h|\varphi_p\rangle + \sum_{oqrs} \langle\tilde{\chi}_\beta|W_{rs}|\varphi_q\rangle P_{qsor}\, (\mathbf{D}^{-1})_{op}\Big]. \tag{19}$$

Introducing matrix notation, this reads

$$\begin{aligned} i\dot{\mathbf{C}} &= i\mathbf{C}\boldsymbol{\eta} + \mathbf{Q}\big(\check{\mathbf{H}} + \check{\mathbf{F}}\mathbf{D}^{-1}\big) \\ &= i\mathbf{C}\boldsymbol{\eta} + \mathbf{Q}\big(\check{\mathbf{H}}\mathbf{D} + \check{\mathbf{F}}\big)\mathbf{D}^{-1}. \end{aligned} \tag{20}$$

The secondary-space projector has matrix elements

$$\begin{aligned} Q_{\alpha\beta} &= \langle\tilde{\chi}_\alpha|Q|\chi_\beta\rangle \\ &= \langle\tilde{\chi}_\alpha|(1-P)|\chi_\beta\rangle \\ &= \langle\tilde{\chi}_\alpha|\chi_\beta\rangle - \sum_p \langle\tilde{\chi}_\alpha|\varphi_p\rangle\,\langle\tilde{\varphi}_p|\chi_\beta\rangle \end{aligned} \tag{21}$$

or simply

$$\mathbf{Q} = \mathbf{1} - \mathbf{C}\tilde{\mathbf{C}}. \tag{22}$$

The matrices $\check{\mathbf{H}}$ and $\check{\mathbf{F}}$ contain half-transformed one-electron integrals,

$$\check{H}_{\beta p} = \langle\tilde{\chi}_\beta|h|\varphi_p\rangle = h_{\beta p}, \tag{23}$$

and half-transformed mean-field elements,

$$\begin{aligned} \check{F}_{\beta o} &= \sum_{qrs}\langle\tilde{\chi}_\beta|W_{rs}|\varphi_q\rangle P_{qsor} \\ &= \sum_{qrs}\int \tilde{\chi}_\beta(\mathbf{x})\left[\int \tilde{\varphi}_r(\mathbf{y})u(\mathbf{x},\mathbf{y})\varphi_s(\mathbf{y})\,\mathrm{d}\mathbf{y}\right]\varphi_q(\mathbf{x})\,\mathrm{d}\mathbf{x}\,P_{qsor} \\ &= \sum_{qrs}\iint \tilde{\chi}_\beta(\mathbf{x})\tilde{\varphi}_r(\mathbf{y})u(\mathbf{x},\mathbf{y})\varphi_q(\mathbf{x})\varphi_s(\mathbf{y})\,\mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{y}\,P_{qsor} \\ &= \sum_{qrs} u_{\beta rqs}P_{qsor}. \end{aligned} \tag{24}$$

Using similar steps, Eq. (9) leads to

$$\begin{aligned} i\dot{\tilde{\mathbf{C}}} &= -i\boldsymbol{\eta}\tilde{\mathbf{C}} - \big(\check{\mathbf{H}}' + \mathbf{D}^{-1}\check{\mathbf{F}}'\big)\mathbf{Q} \\ &= -i\boldsymbol{\eta}\tilde{\mathbf{C}} - \mathbf{D}^{-1}\big(\mathbf{D}\check{\mathbf{H}}' + \check{\mathbf{F}}'\big)\mathbf{Q} \end{aligned} \tag{25}$$

with

$$\check{H}'_{p\beta} = \langle\tilde{\varphi}_p|h|\chi_\beta\rangle = h_{p\beta}, \tag{26}$$

$$\check{F}'_{o\beta} = \sum_{qrs} P_{osqr}u_{qr\beta s}. \tag{27}$$

III. RELATION TO OTHER WORK

In Refs. 5 and 6, the parameter equations were derived (for the biorthogonal case) by assuming the expansions in Eqs. (16) and (17) from the outset. Those derivations also apply to the electronic structure problem (this is an explicit point in Ref. 6), so we should check that they agree with Eqs. (20) and (25). Ignoring notational differences, we need to check that

$$\left[\check{\mathbf{H}}\mathbf{D} + \check{\mathbf{F}}\right]_{\bar{\alpha}\bar{p}} = \langle\tilde{\Psi}|c^\dagger_{\bar{p}}[\tilde{a}_{\bar{\alpha}}, H]|\Psi\rangle, \tag{28}$$

$$\left[\mathbf{D}\check{\mathbf{H}}' + \check{\mathbf{F}}'\right]_{\bar{p}\bar{\alpha}} = \langle\tilde{\Psi}|[H, a^\dagger_{\bar{\alpha}}]\tilde{c}_{\bar{p}}|\Psi\rangle. \tag{29}$$

Here, the operators $a^\dagger_{\bar{\alpha}}$ and $\tilde{a}_{\bar{\alpha}}$ create and annihilate the primitive basis. We note that

$$\{\tilde{a}_{\bar{\alpha}}, c^\dagger_p\} = C_{\bar{\alpha}p}, \tag{30}$$

$$\{\tilde{a}_{\bar{\alpha}}, \tilde{c}_p\} = 0, \tag{31}$$

$$\{\tilde{c}_p, a^\dagger_{\bar{\alpha}}\} = \tilde{C}_{p\bar{\alpha}}, \tag{32}$$

$$\{c^\dagger_p, a^\dagger_{\bar{\alpha}}\} = 0, \tag{33}$$

which implies the following commutators:

$$\begin{aligned}[\tilde{a}_{\bar{\alpha}}, c^\dagger_p\tilde{c}_q] &= \{\tilde{a}_{\bar{\alpha}}, c^\dagger_p\}\tilde{c}_q - c^\dagger_p\{\tilde{a}_{\bar{\alpha}}, \tilde{c}_q\} \\ &= C_{\bar{\alpha}p}\tilde{c}_q\end{aligned} \tag{34}$$

$$\begin{aligned}[c^\dagger_p\tilde{c}_q, a^\dagger_{\bar{\alpha}}] &= -\{c^\dagger_p, a^\dagger_{\bar{\alpha}}\}\tilde{c}_q + c^\dagger_p\{\tilde{c}_q, a^\dagger_{\bar{\alpha}}\} \\ &= c^\dagger_p\tilde{C}_{q\bar{\alpha}}\end{aligned} \tag{35}$$

$$\begin{aligned}[\tilde{a}_{\bar{\alpha}}, c^\dagger_p c^\dagger_q\tilde{c}_s\tilde{c}_r] &= \{\tilde{a}_{\bar{\alpha}}, c^\dagger_p\}c^\dagger_q\tilde{c}_s\tilde{c}_r - c^\dagger_p\{\tilde{a}_{\bar{\alpha}}, c^\dagger_q\}\tilde{c}_s\tilde{c}_r + c^\dagger_p c^\dagger_q\{\tilde{a}_{\bar{\alpha}}, \tilde{c}_s\}\tilde{c}_r - c^\dagger_p c^\dagger_q\tilde{c}_s\{\tilde{a}_{\bar{\alpha}}, \tilde{c}_r\} \\ &= C_{\bar{\alpha}p}c^\dagger_q\tilde{c}_s\tilde{c}_r - C_{\bar{\alpha}q}c^\dagger_p\tilde{c}_s\tilde{c}_r\end{aligned} \tag{36}$$

$$\begin{aligned}[c^\dagger_p c^\dagger_q\tilde{c}_s\tilde{c}_r, a^\dagger_{\bar{\alpha}}] &= -\{c^\dagger_p, a^\dagger_{\bar{\alpha}}\}c^\dagger_q\tilde{c}_s\tilde{c}_r + c^\dagger_p\{c^\dagger_q, a^\dagger_{\bar{\alpha}}\}\tilde{c}_s\tilde{c}_r - c^\dagger_p c^\dagger_q\{\tilde{c}_s, a^\dagger_{\bar{\alpha}}\}\tilde{c}_r + c^\dagger_p c^\dagger_q\tilde{c}_s\{\tilde{c}_r, a^\dagger_{\bar{\alpha}}\} \\ &= -c^\dagger_p c^\dagger_q\tilde{c}_r\tilde{C}_{s\bar{\alpha}} + c^\dagger_p c^\dagger_q\tilde{c}_s\tilde{C}_{r\bar{\alpha}}\end{aligned} \tag{37}$$

The right-hand side of Eq. (28) now becomes

$$\begin{aligned}
\langle\tilde{\Psi}|c^\dagger_{\bar{p}}[\tilde{a}_{\bar{\alpha}}, H]|\Psi\rangle &= \sum_{pq} h_{pq}\langle\tilde{\Psi}|c^\dagger_{\bar{p}}[\tilde{a}_{\bar{\alpha}}, c^\dagger_p\tilde{c}_q]|\Psi\rangle + \frac{1}{2}\sum_{pqrs} u_{pqrs}\langle\tilde{\Psi}|c^\dagger_{\bar{p}}[\tilde{a}_{\bar{\alpha}}, c^\dagger_p c^\dagger_q\tilde{c}_s\tilde{c}_r]|\Psi\rangle \\
&= \sum_{pq} C_{\bar{\alpha}p}h_{pq}\langle\tilde{\Psi}|c^\dagger_{\bar{p}}\tilde{c}_q|\Psi\rangle \\
&\quad + \frac{1}{2}\sum_{pqrs}\Big(C_{\bar{\alpha}p}u_{pqrs}\langle\tilde{\Psi}|c^\dagger_{\bar{p}}c^\dagger_q\tilde{c}_s\tilde{c}_r|\Psi\rangle - C_{\bar{\alpha}q}u_{pqrs}\langle\tilde{\Psi}|c^\dagger_{\bar{p}}c^\dagger_p\tilde{c}_s\tilde{c}_r|\Psi\rangle\Big) \\
&= \sum_{pq} C_{\bar{\alpha}p}h_{pq}\rho_{q\bar{p}} + \frac{1}{2}\sum_{pqrs}\left(C_{\bar{\alpha}p}u_{pqrs}\rho_{rs\bar{p}q} - C_{\bar{\alpha}q}u_{pqrs}\rho_{rs\bar{p}p}\right)
\end{aligned} \tag{38}$$

The last term can be simplified by renaming summation indices ($p \leftrightarrow q$ and $r \leftrightarrow s$) followed by the identities $u_{qpsr} = u_{pqrs}$ and $\rho_{sr\bar{p}q} = -\rho_{rs\bar{p}q}$:

$$\sum_{pqrs} C_{\bar{\alpha}q}u_{pqrs}\rho_{rs\bar{p}p} = \sum_{pqrs} C_{\bar{\alpha}p}u_{qpsr}\rho_{sr\bar{p}q} = -\sum_{pqrs} C_{\bar{\alpha}p}u_{pqrs}\rho_{rs\bar{p}q}. \tag{39}$$

Combining this with Eq. (38) now yields

$$\begin{aligned}
\langle\tilde{\Psi}|c^\dagger_{\bar{p}}[\tilde{a}_{\bar{\alpha}}, H]|\Psi\rangle &= \sum_{pq} C_{\bar{\alpha}p}h_{pq}\rho_{q\bar{p}} + \sum_{pqrs} C_{\bar{\alpha}p}u_{pqrs}\rho_{rs\bar{p}q} \\
&= \sum_{q} h_{\bar{\alpha}q}\rho_{q\bar{p}} + \sum_{qrs} u_{\bar{\alpha}qrs}\rho_{rs\bar{p}q}
\end{aligned} \tag{40}$$

which agrees with Eqs. (24) and (28). In the last step we have used

$$\sum_{p} C_{\bar{\alpha}p}h_{pq} = \sum_{p\beta} C_{\bar{\alpha}p}\tilde{C}_{p\beta}h_{\beta q} = h_{\bar{\alpha}q}. \tag{41}$$

This holds if

$$\sum_{p\beta} C_{\bar{\alpha}p}\tilde{C}_{p\beta} = \delta_{\bar{\alpha}\beta}, \tag{42}$$

which is *not* true if the p summation runs over active (occupied and virtual) orbitals. However, since the primitive basis is finite, we are free to temporarily introduce the secondary basis (i.e. the complement of the active basis) explicitly. This means that $\mathbf{C}$ and $\tilde{\mathbf{C}}$ become square (rather than rectangular) matrices:

$$\mathbf{C} = \left[\begin{array}{c}\mathbf{C}_\mathrm{A}\end{array}\right] \to \left[\begin{array}{c|c}\mathbf{C}_\mathrm{A} & \mathbf{C}_\mathrm{S}\end{array}\right] \tag{43}$$

$$\tilde{\mathbf{C}} = \left[\begin{array}{c}\tilde{\mathbf{C}}_\mathrm{A}\end{array}\right] \to \left[\begin{array}{c}\tilde{\mathbf{C}}_\mathrm{A} \\ \hline \tilde{\mathbf{C}}_\mathrm{S}\end{array}\right] \tag{44}$$

Since the full matrices are square we get that biorthogonality ($\tilde{\mathbf{C}}\mathbf{C} = \mathbf{1}$) implies $\mathbf{C}\tilde{\mathbf{C}} = \mathbf{1}$, which is exactly Eq. (42). We will never actually construct the secondary basis; we only need its *existence* to complete the proof. A similar derivation shows that

$$\langle\tilde{\Psi}|[H, a^\dagger_{\bar{\alpha}}]\tilde{c}_{\bar{p}}|\Psi\rangle = \sum_{p} \rho_{\bar{p}p} h_{p\bar{\alpha}} + \sum_{pqs} \rho_{\bar{p}spq} u_{pq\bar{\alpha}s}, \tag{45}$$

which agrees with Eqs. (27) and (29).

- Orthogonal case?
- Ground state in exponential parameterization?
- Detailed derivation (also vibrational case).

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