

## Relating orbital and parameter equations

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## I. NOTATION

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

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

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

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

Density matrices are defined as

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

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

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

$$u_{pqrs} = u_{qpsr}, \quad (6)$$

$$\rho_{rspq} = \rho_{srqp}. \quad (7)$$

## II. CONVERTING ORBITAL EQUATIONS TO PARAMETER EQUATIONS

The orbital equations are formally identical for all orbital-adaptive methods. Following Kvaal<sup>1</sup> and Sato<sup>2</sup>, they take the appearance

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

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

The mean-field operator<sup>3,4</sup>  $W_{rs}$  is a multiplicative/local operator given by

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

Kvaal<sup>1</sup> uses a slightly different notation, but the meaning should be the same. The secondary-space projector is given by

$$Q = 1 - \sum_p |\varphi_p\rangle \langle \tilde{\varphi}_p|. \quad (11)$$

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

$$D_{qp} = \rho_{qp}, \quad (12)$$

$$P_{rspq} = \rho_{rspq}. \quad (13)$$

In the orthogonal case, the densities are Hermitianized according to

$$D_{qp} = \frac{1}{2}(\rho_{qp} + \rho_{pq}^*), \quad (14)$$

$$P_{rspq} = \frac{1}{2}(\rho_{rspq} + \rho_{pqrs}^*). \quad (15)$$

Having an 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

$$|\varphi_p\rangle = \sum_\alpha |\chi_\alpha\rangle C_{\alpha p}, \quad (16)$$

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

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

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

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

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

Introducing matrix notation, this reads

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

The secondary-space projector has matrix elements

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

or simply

$$\mathbf{Q} = \mathbf{1} - \mathbf{C}\tilde{\mathbf{C}}. \quad (22)$$

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

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

and half-transformed mean-field elements,

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

Using similar steps, Eq. (9) leads to

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

with

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

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

### 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

$$[\check{\mathbf{H}}\mathbf{D} + \check{\mathbf{F}}]_{\bar{\alpha}\bar{p}} = \langle \tilde{\Psi} | c_{\bar{p}}^\dagger [\tilde{a}_{\bar{\alpha}}, H] | \Psi \rangle, \quad (28)$$

$$[\mathbf{D}\check{\mathbf{H}}' + \check{\mathbf{F}}']_{\bar{p}\bar{\alpha}} = \langle \tilde{\Psi} | [H, a_{\bar{\alpha}}^\dagger] \tilde{c}_{\bar{p}} | \Psi \rangle. \quad (29)$$

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

$$\{\tilde{a}_{\bar{\alpha}}, c_p^\dagger\} = C_{\bar{\alpha}p}, \quad (30)$$

$$\{\tilde{a}_{\bar{\alpha}}, \tilde{c}_p\} = 0, \quad (31)$$

$$\{\tilde{c}_p, a_{\bar{\alpha}}^\dagger\} = \tilde{C}_{p\bar{\alpha}}, \quad (32)$$

$$\{c_p^\dagger, a_{\bar{\alpha}}^\dagger\} = 0, \quad (33)$$

which implies the following commutators:

$$\begin{aligned} [\tilde{a}_{\bar{\alpha}}, c_p^\dagger \tilde{c}_q] &= \{\tilde{a}_{\bar{\alpha}}, c_p^\dagger\} \tilde{c}_q - c_p^\dagger \{\tilde{a}_{\bar{\alpha}}, \tilde{c}_p\} \\ &= C_{\bar{\alpha}p} \tilde{c}_q \end{aligned} \quad (34)$$

$$\begin{aligned} [\tilde{a}_{\bar{\alpha}}, c_p^\dagger c_q^\dagger \tilde{c}_s \tilde{c}_r] &= \{\tilde{a}_{\bar{\alpha}}, c_p^\dagger\} c_q^\dagger \tilde{c}_s \tilde{c}_r - c_p^\dagger \{\tilde{a}_{\bar{\alpha}}, c_q^\dagger\} \tilde{c}_s \tilde{c}_r + c_p^\dagger c_p^\dagger \{\tilde{a}_{\bar{\alpha}}, \tilde{c}_s\} \tilde{c}_r - c_p^\dagger c_p^\dagger \tilde{c}_s \{\tilde{a}_{\bar{\alpha}}, \tilde{c}_r\} \\ &= C_{\bar{\alpha}p} c_q^\dagger \tilde{c}_s \tilde{c}_r - C_{\bar{\alpha}q} c_p^\dagger \tilde{c}_s \tilde{c}_r \end{aligned} \quad (35)$$

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

$$\langle \tilde{\Psi} | c_{\bar{p}}^\dagger [\tilde{a}_{\bar{\alpha}}, H] | \Psi \rangle = \sum_{pq} h_{pq} \langle \tilde{\Psi} | c_{\bar{p}}^\dagger [\tilde{a}_{\bar{\alpha}}, c_p^\dagger \tilde{c}_q] | \Psi \rangle + \frac{1}{2} \sum_{pqrs} u_{pqrs} \langle \tilde{\Psi} | c_{\bar{p}}^\dagger [\tilde{a}_{\bar{\alpha}}, c_p^\dagger c_q^\dagger \tilde{c}_s \tilde{c}_r] | \Psi \rangle \quad (36)$$

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