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A Hartree–Fock–Roothaan analogon using the principle of variance minimization

I. A Roothaan-like equation minimizing variance

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The variance expression $\|\boldsymbol{H}\Psi-\lambda^*\cdot\Psi\|^2$, which gives an upper bound for the distance between the real number λ^* and the spectrum of the Schrödinger operator $\boldsymbol{H}$, is computed for a closed-shell Slater determinant Ψ. A Roothaan-like matrix equation is deduced for the determination of variance-minimizing orbitals.

Key words. Eigenvalue problems.

1. Introduction

Variance Minimization [1, 2] has been shown to provide good lower bounds for the lower eigenvalues of $^{\infty}$He [3, 4], ^{4}He [5], and some other three-particle systems [6]. The procedure does not yield absolute lower bounds, but rather an interval enclosing at least one eigenvalue; on the other hand it has the advantages of a variational procedure, where basis functions may be chosen arbitrarily.

It seems desirable to extend this method to many-particle systems, with the wavefunction expressed in terms of Slater determinants. In this paper, as one step towards this goal, the variance expression, $\|\boldsymbol{H}\Psi-\lambda^*\cdot\Psi\|$, will be computed for Ψ as a single closed-shell Slater determinant. Minimization of this expression with respect to a given basis will lead to a matrix equation similar to the Roothaan equation, but yielding variance-minimizing rather than energy-minimizing orbitals.

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2. $\|\boldsymbol{H}\Psi\|^2$ for Slater determinants

The distance between an arbitrary real number λ^* (e.g. a Ritz or Hartree–Fock value) and the spectrum σ of the Schrödinger operator $\boldsymbol{H}$ may be estimated by

$$\inf_{\lambda\in\sigma(\boldsymbol{H})}|\lambda-\lambda^*|^2\leq\|\boldsymbol{H}\Psi-\lambda^*\cdot\Psi\|^2,$$

where Ψ may be any normalized function in the domain of $\boldsymbol{H}$. Thus the first step of Variance Minimization consists in minimizing $\|\boldsymbol{H}\Psi-\lambda^*\cdot\Psi\|^2$ with respect to a given λ^* by varying Ψ.

Since, for a normalized Ψ,

$$\|\boldsymbol{H}\Psi-\lambda^*\cdot\Psi\|^2=\langle\boldsymbol{H}\Psi|\boldsymbol{H}\Psi\rangle-2\lambda^*\langle\boldsymbol{H}\Psi|\Psi\rangle+\lambda^{*2},$$

we see that, in order to calculate $\|\boldsymbol{H}\Psi-\lambda^*\cdot\Psi\|^2$ for a Slater determinant, we have to express not only the energy value $\langle\boldsymbol{H}\Psi|\Psi\rangle$, but also $\langle\boldsymbol{H}\Psi|\boldsymbol{H}\Psi\rangle=\|\boldsymbol{H}\Psi\|^2$ as a functional of the occupied orbitals.

As in the Hartree–Fock calculation of $\langle\boldsymbol{H}\Psi|\Psi\rangle$ (see, e.g. [7]) we start decomposing $\boldsymbol{H}$ into a sum of one- and two-electron operators.

For the considered closed-shell atomic system of $2n$ electrons and nuclear charge Z,

$$\boldsymbol{H}=\boldsymbol{H}_1+\boldsymbol{H}_2$$

with

$$\boldsymbol{H}_1=\sum_{p=1}^{2n}H_p,\qquad H_p=-\tfrac{1}{2}\nabla_p^2-\frac{Z}{r_p},$$

$$\boldsymbol{H}_2=\sum_{p<q}\sum\frac{1}{r_{pq}}.$$

In this way, $\langle\boldsymbol{H}\Psi|\boldsymbol{H}\Psi\rangle$ decomposes into

$$\underset{(\mathscr{A})}{\langle\boldsymbol{H}_1\Psi|\boldsymbol{H}_1\Psi\rangle}+\underset{(\mathscr{B})}{2\langle\boldsymbol{H}_1\Psi\boldsymbol{H}_2\Psi\rangle}+\underset{(\mathscr{C})}{\langle\boldsymbol{H}_2\Psi|\boldsymbol{H}_2\Psi\rangle}$$

where

$$\begin{aligned}\langle\boldsymbol{H}_1\Psi|\boldsymbol{H}_1\Psi\rangle&=\sum_{p,q=1}^{2n}\sum\langle H_p\Psi|H_q\Psi\rangle=2n\cdot\sum_{q=1}^{2n}\langle H_1\Psi|H_q\Psi\rangle\\&=2n\cdot\langle H_1\Psi|H_1\Psi\rangle&&(\mathscr{A}1)\\&\quad+2n(2n-1)\cdot\langle H_1\Psi|H_2\Psi\rangle&&(\mathscr{A}2);\end{aligned}$$

$$\begin{aligned}\langle\boldsymbol{H}_1\Psi|\boldsymbol{H}_2\Psi\rangle&=\sum_{p=1}^{2n}\sum_{q<s}\sum\left\langle H_p\Psi\middle|\frac{1}{r_{qs}}\Psi\right\rangle=2n\cdot\sum_{q<s}\sum\left\langle H_1\Psi\middle|\frac{1}{r_{qs}}\Psi\right\rangle\\&=2n(2n-1)\cdot\left\langle H_1\Psi\middle|\frac{1}{r_{12}}\Psi\right\rangle&&(\mathscr{B}1)\\&\quad+\frac{1}{2}\cdot2n(2n-1)(2n-2)\cdot\left\langle H_1\Psi\middle|\frac{1}{r_{23}}\Psi\right\rangle&&(\mathscr{B}2);\end{aligned}$$

$$\langle \boldsymbol{H}_2\Psi|\boldsymbol{H}_2\Psi\rangle = \sum_{p<q}\sum\sum_{s<t}\sum \left\langle \frac{1}{r_{pq}}\Psi \middle| \frac{1}{r_{st}}\Psi \right\rangle = \tfrac{1}{2}\cdot 2n(2n-1)\cdot \sum_{s<t}\sum \left\langle \frac{1}{r_{12}}\Psi \middle| \frac{1}{r_{st}}\Psi \right\rangle$$

$$= \tfrac{1}{2}\cdot 2n(2n-1)\cdot \left\langle \frac{1}{r_{12}}\Psi \middle| \frac{1}{r_{12}}\Psi \right\rangle \qquad (\mathscr{C}1)$$

$$+ 2n(2n-1)(2n-2)\cdot \left\langle \frac{1}{r_{12}}\Psi \middle| \frac{1}{r_{23}}\Psi \right\rangle \qquad (\mathscr{C}2)$$

$$+ \tfrac{1}{4}\cdot 2n(2n-1)(2n-1)(2n-2)(2n-3)\cdot \left\langle \frac{1}{r_{12}}\Psi \middle| \frac{1}{r_{34}}\Psi \right\rangle \qquad (\mathscr{C}3).$$

On inserting for Ψ a normalized Slater determinant,

$$\Psi = \frac{1}{\sqrt{(2n)!}}\cdot \sum_{\mu} p_\mu \cdot \boldsymbol{P}_\mu\{\psi_1\alpha(1)\psi_1\beta(2)\psi_2\alpha(3)\cdots\psi_n\beta(2n)\},$$

$$p_\mu = \begin{cases} -1 & \text{for odd permutations } \boldsymbol{P}_\mu \text{ and} \\ +1 & \text{for even ones,} \end{cases}$$

$\langle \boldsymbol{H}\Psi|\boldsymbol{H}\Psi\rangle$ decomposes into a double sum over the permutations:

$$\langle \boldsymbol{H}\Psi|\boldsymbol{H}\Psi\rangle = \frac{1}{(2n)!}\cdot \sum_{\mu}\sum_{\nu} p_\mu p_\nu \cdot \langle \boldsymbol{H}\boldsymbol{P}_\mu\{\psi_1\alpha\cdots\psi_n\beta\}|\boldsymbol{H}\boldsymbol{P}_\nu\{\psi_1\alpha\cdots\psi_n\beta\}\rangle,$$

and so do all the summands $\mathscr{A}1$–$\mathscr{C}3$.

In each of these double sums, in the same way as in the Hartree–Fock calculation of $\langle \boldsymbol{H}\Psi|\Psi\rangle$, terms will vanish on account of the orthogonality of the spinorbitals. They vanish if $\boldsymbol{P}_\mu$ and $\boldsymbol{P}_\nu$ assign different orbitals to an electron which, in this very term, is not affected by an operator, or if $\boldsymbol{P}_\mu$ and $\boldsymbol{P}_\nu$ assign different spins to any electron.

This means that, in each of the summands $\mathscr{A}1$–$\mathscr{C}3$, $\boldsymbol{P}_\mu$ and $\boldsymbol{P}_\nu$ may differ only by a permutation of those electrons affected by an operator. In case they differ by any such permutation at all, the "permuted" electrons must have the same spin.

In $\mathscr{A}1$, the permutations $\boldsymbol{P}_\mu$ and $\boldsymbol{P}_\nu$ have to be the same:

$$\mathscr{A}1 = 2n\cdot\frac{1}{(2n)!}\cdot\sum_{\mu}\langle H_1\boldsymbol{P}_\mu\{\psi_1\alpha\cdots\psi_n\beta\}|H_1\boldsymbol{P}_\mu\{\psi_1\alpha\cdots\psi_n\beta\}\rangle.$$

The $(2n-1)!$ permutations assigning the same spinorbital $\psi_i\sigma_i$ to electron 1 all lead to the same value, thus making up for the normalization factor. The summands in which electron 1 is assigned $\psi_i\alpha$ and $\psi_i\beta$ are equal; so

$$\mathscr{A}1 = 2\sum_{i=1}^{n}\int |H_1\psi_i(1)|^2\, d\tau_1.$$

Let us introduce the following inner product notation for integrals over the coordinates of one or more electrons:

Each orbital ψ_i will be represented by its index i, the LCAO basis functions ϕ_{i_1} in the next chapter by an index i_1; thus an integral

$$\int \bar{\psi}_i(1)\bar{\psi}_j(2)\cdots\cdot A\psi_k(1)\psi_l(2)\cdots d\tau_1\, d\tau_2\cdots$$

will be written

$$\langle ij\cdots|Akl\cdots\rangle$$

or, if the operator A is symmetric,

$$\langle ij\cdots|A|kl\cdots\rangle.$$

Operators signed by an index $1, 2, \ldots$ are meant to act upon the first, second, ... electron of the product in which they are written. Thus an integral

$$\int \bar{\psi}_i(3)\bar{\psi}_j(4)\cdot\frac{1}{r_{34}}\cdot\psi_k(3)\psi_l(4)\, d\tau_3\, d\tau_4$$

will be abbreviated as

$$\langle ij|\frac{1}{r_{12}}|kl\rangle.$$

Variation will be indicated by a circumflex; e.g.

$$\langle i\hat{j}|\frac{1}{r_{12}}|kl\rangle$$

will denote a Coulomb-type product involving a variation of the orbital $\psi_j(2)$.

In this notation, our first summand is

$$\mathscr{A}1=2\sum_{i=1}^{n}\langle i|H^2|i\rangle.$$

In $\mathscr{A}2$, $\mathscr{B}2$, and $\mathscr{C}1$, $\boldsymbol{P}_\mu$ and $\boldsymbol{P}_\nu$ may be the same, or differ by the permutation (12). If $\boldsymbol{P}_\mu=\boldsymbol{P}_\nu$, there are 4 possible spin combinations if the electrons 1 and 2 are assigned different orbitals $\psi_i\neq\psi_j$, or 2 spin combinations if they are assigned the same orbital ψ_i. In case $\boldsymbol{P}_\nu=(12)\cdot\boldsymbol{P}_\mu$, electrons 1 and 2 must have the same spin (2 possibilities) and different orbitals; these "exchange-type" terms enter with negative sign since $p_\mu\cdot p_\nu=-1$.

There are $(2n-2)!$ permutations assigning to the electrons 1 and 2 the same combination of spinorbitals (thus the normalization factor cancels out again):

$$\begin{aligned}\mathscr{A}2&=4\sum_{i\neq j}\sum\langle i|H|i\rangle\cdot\langle j|H|j\rangle+2\sum_{i}\langle i|H|i\rangle^2-2\sum_{i\neq j}\sum\langle i|H|j\rangle^2\\&=\sum_{i,j=1}^{n}\sum(4\langle i|H|i\rangle\cdot\langle j|H|j\rangle-2\langle i|H|j\rangle^2);\end{aligned}$$

$$\mathscr{B}1=\sum_{i,j=1}^{n}\sum\left(4\left\langle\frac{H_1}{r_{12}}\,ij\,\middle|\,ij\right\rangle-2\left\langle\frac{H_1}{r_{12}}\,ij\,\middle|\,ji\right\rangle\right)$$

(H_1/r_{12}) here means: apply the one-electron hamiltonian H on the first orbital, then divide by r_{12});

$$\mathscr{C}1=\sum_{i,j=1}^{n}\sum\left(2\langle ij|\frac{1}{r_{12}^2}|ij\rangle-\langle ij|\frac{1}{r_{12}^2}|ji\rangle\right).$$

In $\mathscr{B}2$ and $\mathscr{C}2$, $\boldsymbol{P}_\mu$ and $\boldsymbol{P}_\nu$ may

* be the same
giving at most 8 spin combinations, with $p_\mu\cdot p_\nu=+1$ or
* differ by an interchange (12), (13), or (23)
giving at most 4 spin combinations, with $p_\mu\cdot p_\nu=-1$ or
* differ by (123) or (132)
giving 2 spin combinations (provided all ψ are different) with $p_\mu\cdot p_\nu=+1$.

Note that the three interchanges (12), (13), and (23) do not give the same results; for example, in

$$\left\langle H_1\Psi\,\middle|\,\frac{1}{r_{23}}\Psi\right\rangle$$

(12) and (13) are equivalent, while (23) will give a different result.

Noting well the reduction of possible spin combinations in case two orbitals are equal, we find

$$\begin{aligned}\mathscr{B}2=\sum_{i,j,k=1}^{n}\sum\sum\, & 4\langle i|H|i\rangle\cdot\langle jk|\frac{1}{r_{12}}|jk\rangle-4\langle i|H|j\rangle\cdot\langle jk|\frac{1}{r_{12}}|ik\rangle\\ & -2\langle i|H|i\rangle\cdot\langle jk|\frac{1}{r_{12}}|kj\rangle+2\langle i|H|j\rangle\cdot\langle jk|\frac{1}{r_{12}}|ki\rangle\end{aligned}$$

and

$$\begin{aligned}\mathscr{C}2=\sum_{i,j,k=1}^{n}\sum\sum\, & 8\langle ijk|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|ijk\rangle-8\,\langle ijk|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|jik\rangle\\ & -4\,\langle ijk|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|kji\rangle+4\,\langle ijk|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|kij\rangle.\end{aligned}$$

In $\mathscr{C}3$, the last summand of $\|\boldsymbol{H}\Psi\|^2$, $\boldsymbol{P}_\mu$ and $\boldsymbol{P}_\nu$ may differ by any of the 24 possible permutations of electrons 1–4:

$$\begin{aligned}\mathscr{C}3=\sum_{i,j,k,l=1}^{n}\sum\sum\sum\, & 4\,\langle ij|\frac{1}{r_{12}}|ij\rangle\cdot\langle kl|\frac{1}{r_{12}}|kl\rangle-4\,\langle ij|\frac{1}{r_{12}}|ji\rangle\cdot\langle kl|\frac{1}{r_{12}}|kl\rangle\\ & -8\,\langle ij|\frac{1}{r_{12}}|kj\rangle\cdot\langle kl|\frac{1}{r_{12}}il\rangle+8\,\langle ij|\frac{1}{r_{12}}|ki\rangle\cdot\langle kl|\frac{1}{r_{12}}|jl\rangle\end{aligned}$$

$$+\langle ij|\frac{1}{r_{12}}|ji\rangle\cdot\langle kl|\frac{1}{r_{12}}|lk\rangle+2\langle ij|\frac{1}{r_{12}}|kl\rangle^2$$

$$-2\langle ij|\frac{1}{r_{12}}|ki\rangle\cdot\langle kl|\frac{1}{r_{12}}|lj\rangle-\langle ij|\frac{1}{r_{12}}|kl\rangle\cdot\langle kl|\frac{1}{r_{12}}|ji\rangle.$$

3. Minimization of $\|H\Psi-\lambda^*\cdot\Psi\|^2$

Combining the results $\mathscr{A}1$–$\mathscr{C}3$ with the familiar Hartree–Fock energy expression, we get the variance expression for a closed-shell Slater determinant,

$$F^2(\Psi;\lambda^*)=\|H\Psi\|^2-2\lambda^*\cdot\langle H\Psi|\Psi\rangle+\lambda^{*2}$$

$$\begin{aligned}
&=\sum\sum\sum\sum_{i,j,k,l=1}^{n}4\langle ij|\frac{1}{r_{12}}|ij\rangle\cdot\langle kl|\frac{1}{r_{12}}|kl\rangle\\
&\quad-4\langle ij|\frac{1}{r_{12}}|ji\rangle\cdot\langle kl|\frac{1}{r_{12}}|kl\rangle\\
&\quad-8\langle ij|\frac{1}{r_{12}}|kj\rangle\cdot\langle kl|\frac{1}{r_{12}}|il\rangle+8\langle ij|\frac{1}{r_{12}}|ki\rangle\cdot\langle kl|\frac{1}{r_{12}}|jl\rangle\\
&\quad+\langle ij|\frac{1}{r_{12}}|ji\rangle\cdot\langle kl|\frac{1}{r_{12}}|lk\rangle+2\langle ij|\frac{1}{r_{12}}|kl\rangle^2\\
&\quad-2\langle ij|\frac{1}{r_{12}}|ki\rangle\cdot\langle kl|\frac{1}{r_{12}}|lj\rangle-\langle ij|\frac{1}{r_{12}}|kl\rangle\cdot\langle kl|\frac{1}{r_{12}}|ji\rangle\\
&\quad+\sum\sum\sum_{i,j,k=1}^{n}8\langle ijk|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|ijk\rangle-8\langle ijk|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|jik\rangle\\
&\quad-4\langle ijk|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|kji\rangle+4\langle ijk|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|kij\rangle\\
&\quad+8\langle i|H|i\rangle\cdot\langle jk|\frac{1}{r_{12}}|jk\rangle\\
&\quad-8\langle i|H|j\rangle\cdot\langle jk|\frac{1}{r_{12}}|ik\rangle-4\langle i|H|i\rangle\cdot\langle jk|\frac{1}{r_{12}}|kj\rangle\\
&\quad+4\langle i|H|j\rangle\cdot\langle jk|\frac{1}{r_{12}}|ki\rangle\\
&\quad+\sum\sum_{i,j=1}^{n}2\langle ij|\frac{1}{r_{12}^2}|ij\rangle-\langle ij|\frac{1}{r_{12}^2}|ji\rangle\\
&\quad+8\langle\frac{H_1}{r_{12}}ij|ij\rangle-4\langle\frac{H_1}{r_{12}}ij|ji\rangle+4\langle i|H|i\rangle\cdot\langle j|H|j\rangle
\end{aligned}$$

$$-2\langle i|H|j\rangle^2-4\lambda^*\cdot\langle ij|\frac{1}{r_{12}}|ij\rangle+2\lambda^*\cdot\langle ij|\frac{1}{r_{12}}|ji\rangle$$

$$+\sum_{i=1}^{n}2\langle i|H^2|i\rangle-4\lambda^*\cdot\langle i|H|i\rangle+\lambda^{*2}.$$

This has to be minimized by varying the orbitals ψ, with the constraints that the orbitals stay orthonormal.

As in the Hartree–Fock procedure, the constraints are introduced by means of Lagrange multipliers [8]; let us call them $-2\chi_{ij}$. We get an auxiliary functional

$$\Phi=F^2-2\sum_i\sum_j\chi_{ij}\cdot(\langle i|j\rangle-\delta_{ij})\qquad(\delta_{ij}\text{: Kronecker delta})$$

to be minimized without constraints.

On the same reasons as in Hartree–Fock calculation, we may choose the orbitals such that the χ_{ij} vanish for $i\neq j$.

For the following calculations, let us assume that all inner products are real—as it is the case for atomic systems if we use orbitals composed of spherical harmonics and real-valued functions.

The variation $\hat{\Phi}$ of the auxiliary functional is formed by varying, one after the other, each orbital ψ_i, ψ_j, . . . in each of the products:

$$\hat{\Phi}=\sum_{ijkl}\sum\sum\sum 4\langle \hat{i}j|\frac{1}{r_{12}}|ij\rangle\cdot\langle kl|\frac{1}{r_{12}}|kl\rangle+4\langle i\hat{j}|\frac{1}{r_{12}}|ij\rangle\cdot\langle kl|\frac{1}{r_{12}}|kl\rangle$$

$$+4\langle ij|\frac{1}{r_{12}}|\hat{i}j\rangle\cdot\langle kl|\frac{1}{r_{12}}|kl\rangle+\cdots$$

and renaming the sums in such a way that the orbital which is being varied is given the index i.

Note that, different from the corresponding Hartree–Fock calculations, variation of different orbitals in the same partial sum does not always lead to equal results; e.g.

$$\sum_{ijkl}\sum\sum\sum\langle\hat{i}j|\frac{1}{r_{12}}|ji\rangle\cdot\langle kl|\frac{1}{r_{12}}|kl\rangle\neq\sum_{ijkl}\sum\sum\sum\langle ij|\frac{1}{r_{12}}|ji\rangle\cdot\langle\hat{k}l|\frac{1}{r_{12}}|kl\rangle.$$

In terms involving H_1/r_{12}, we must further be aware that this operator is not symmetric (only $(H_1+H_2)/r_{12}$ will be); for example,

$$\left\langle\frac{H_1}{r_{12}}\hat{i}j\right\rangle\neq\left\langle\frac{H_1}{r_{12}}ij\middle|\hat{i}j\right\rangle.$$

The condition that $\hat{\Phi}$ has to be zero for any variation $\hat{\psi}_i$ of any orbital ψ_i leads to a Hartree–Fock-like equation

$$Q\psi_i=\chi_i\cdot\psi_i$$

with the one-electron operator Q itself depending on the occupied orbitals ψ_i in a similar (though more complicated) way as the Fock operator F in the Hartree–Fock equation.

4. Linear ansatz of the orbitals

By an ansatz of the orbitals as linear combinations of m basis functions ϕ_{i_1},

$$\psi_i = \sum_{i_1=1}^{m} c_{i,i_1} \cdot \phi_{i_1},$$

the functional $\|\boldsymbol{H}\Psi - \lambda^* \cdot \Psi\|^2$ becomes an ordinary function of the coefficient vectors $\boldsymbol{c}_i$, and minimization leads to a Roothaan-like matrix equation

$$Q\boldsymbol{c}_i = \chi_i \cdot S\boldsymbol{c}_i,$$

where S is the overlap matrix with the element

$$S_{i_1,i_2} = \langle i_1 | i_2 \rangle$$

and the element of Q is

$$Q_{i_1,i_2} = Q^{(1)}_{i_1,i_2} + Q^{(2)}_{i_1,i_2} + Q^{(3)}_{i_1,i_2} + Q^{(4)}_{i_1,i_2}$$

with

$$Q^{(1)}_{i_1,i_2} = \langle i_1 | H^2 | i_2 \rangle - 2\lambda^* \cdot \langle i_1 | H | i_2 \rangle,$$

$$Q^{(2)}_{i_1,i_2} = \sum_{j_1=1}^{m} \sum_{j_2=1}^{m} P_{j_1,j_2}$$

$$\left\{ \begin{array}{l}
\langle i_1 j_1 | \frac{1}{r_{12}^2} | i_2 j_2 \rangle - \tfrac{1}{2} \langle i_1 j_1 | \frac{1}{r_{12}^2} | j_2 i_2 \rangle + \left\langle \frac{H_1}{r_{12}}\, i_1 j_1 \middle| i_2 j_2 \right\rangle \\
+ \left\langle \frac{H_1}{r_{12}}\, j_1 i_1 \middle| j_2 i_2 \right\rangle + \left\langle i_1 j_1 \middle| \frac{H_1}{r_{12}}\, i_2 j_2 \right\rangle + \left\langle j_1 i_1 \middle| \frac{H_1}{r_{12}}\, j_2 i_2 \right\rangle \\
\times \; -\frac{1}{2} \left\langle \frac{H_1}{r_{12}}\, i_1 j_1 \middle| j_2 i_2 \right\rangle - \frac{1}{2} \left\langle \frac{H_1}{r_{12}}\, j_1 i_1 \middle| i_2 j_2 \right\rangle - \frac{1}{2} \left\langle i_1 j_1 \middle| \frac{H_1}{r_{12}}\, j_2 i_2 \right\rangle \\
-\frac{1}{2} \left\langle j_1 i_1 \middle| \frac{H_1}{r_{12}}\, i_2 j_2 \right\rangle \\
+ 2\langle i_1 | H | i_2 \rangle \cdot \langle j_1 | H | j_2 \rangle - \langle i_1 | H | j_2 \rangle \cdot \langle j_1 | H | i_2 \rangle \\
- 2\lambda^* \cdot \langle i_1 j_1 | \frac{1}{r_{12}} | i_2 j_2 \rangle + \lambda^* \cdot \langle i_1 j_1 | \frac{1}{r_{12}} | j_2 i_2 \rangle,
\end{array} \right.$$

$$Q^{(3)}_{i_1,i_2}=\sum_{j_1,k_1=1}^{m}\sum\sum_{j_2,k_2=1}^{m} P_{j_1,j_2}\cdot P_{k_1,k_2}$$

$$\left\{\begin{aligned}
&2\langle i_1j_1k_1|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|i_2j_2k_2\rangle\\
&-\langle i_1j_1k_1|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|j_2i_2k_2\rangle-\langle i_1j_1k_1|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|i_2k_2j_2\rangle\\
&-\langle i_1j_1k_1|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|k_2j_2i_2\rangle\\
&+\tfrac{1}{2}\langle i_1j_1k_1|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|k_2i_2j_2\rangle\\
&+\tfrac{1}{2}\langle i_1j_1k_1|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|j_2k_2i_2\rangle+\langle j_1i_1k_1|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|j_2i_2k_2\rangle\\
&-\langle j_1i_1k_1|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|i_2j_2k_2\rangle\\
&-\tfrac{1}{2}\langle j_1i_1k_1|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|k_2i_2j_2\rangle\\
&+\tfrac{1}{2}\langle j_1i_1k_1|\frac{1}{r_{12}}\cdot\frac{1}{r_{23}}|k_2j_2i_2\rangle+\langle i_1|H|i_2\rangle\cdot\langle j_1k_1|\frac{1}{r_{12}}|j_2k_2\rangle\\
&-\langle i_1|H|j_2\rangle\cdot\langle j_1k_1|\frac{1}{r_{12}}|i_2k_2\rangle\\
&-\tfrac{1}{2}\langle i_1|H|i_2\rangle\cdot\langle j_1k_1|\frac{1}{r_{12}}|k_2j_2\rangle\\
&+\tfrac{1}{2}\langle i_1|H|j_2\rangle\cdot\langle j_1k_1|\frac{1}{r_{12}}|k_2j_2\rangle\\
&+2\langle i_1j_1|\frac{1}{r_{12}}|i_2j_2\rangle\cdot\langle k_1|H|k_2\rangle\\
&-\langle i_1j_1|\frac{1}{r_{12}}|k_2j_2\rangle\cdot\langle k_1|H|i_2\rangle-\langle i_1j_1|\frac{1}{r_{12}}|i_2k_2\rangle\cdot\langle k_1|H|j_2\rangle\\
&-\langle i_1j_1|\frac{1}{r_{12}}|j_2i_2\rangle\cdot\langle k_1|H|k_2\rangle\\
&+\tfrac{1}{2}\langle i_1j_1|\frac{1}{r_{12}}|j_2k_2\rangle\cdot\langle k_1|H|i_2\rangle\\
&+\tfrac{1}{2}\langle i_1j_1|\frac{1}{r_{12}}|k_2i_2\rangle\cdot\langle k_1|H|j_2\rangle,
\end{aligned}\right.$$

and

$$
Q^{(4)}_{i_2,i_2} = \sum^{m}_{j_1,k_1,l_1=1}\sum\sum \; \sum^{m}_{j_2,k_2,l_2=1}\sum\sum P_{j_1,j_2} \cdot P_{k_1,k_2} \cdot P_{l_1,l_2}
\left\{
\begin{aligned}
& \langle i_1 j_1|\frac{1}{r_{12}}|i_2 j_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|k_2 l_2\rangle \\
& -\tfrac{1}{2}\langle i_1 j_1|\frac{1}{r_{12}}|j_2 i_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|k_2 l_2\rangle \\
& -\tfrac{1}{2}\langle i_1 j_1|\frac{1}{r_{12}}|i_2 j_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|l_2 k_2\rangle - \langle i_1 j_1|\frac{1}{r_{12}}|k_2 l_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|i_2 l_2\rangle \\
& -\langle i_1 j_1|\frac{1}{r_{12}}|i_2 k_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|j_2 l_2\rangle \\
& +\tfrac{1}{2}\langle i_1 j_1|\frac{1}{r_{12}}|k_2 j_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|j_2 l_2\rangle \\
& +\tfrac{1}{2}\langle i_1 j_1|\frac{1}{r_{12}}|j_2 k_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|i_2 l_2\rangle \\
& +\tfrac{1}{2}\langle i_1 j_1|\frac{1}{r_{12}}|k_2 j_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|l_2 i_2\rangle \\
& +\tfrac{1}{2}\langle i_1 j_1|\frac{1}{r_{12}}|i_2 k_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|l_2 j_2\rangle \\
& +\tfrac{1}{4}\langle i_i j_1|\frac{1}{r_{12}}|j_2 i_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|l_2 k_2\rangle \\
& +\tfrac{1}{2}\langle i_1 j_1|\frac{1}{r_{12}}|k_2 l_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|i_2 j_2\rangle \\
& -\tfrac{1}{4}\langle i_1 j_1|\frac{1}{r_{12}}|k_2 i_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|l_2 j_2\rangle \\
& -\tfrac{1}{4}\langle i_1 j_1|\frac{1}{r_{12}}|j_2 k_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|l_2 i_2\rangle \\
& -\tfrac{1}{4}\langle i_1 j_1|\frac{1}{r_{12}}|k_2 l_2\rangle \cdot \langle k_1 l_1|\frac{1}{r_{12}}|j_2 i_2\rangle ,
\end{aligned}
\right.
$$

where P_{i_1,i_2} is the element of the usual density matrix,

$$P_{i_1,i_2} = \sum_{i=1}^{n} 2c_{i,i_1} \cdot c_{i,i_2},$$

with c_{i,i_1} the i_1th component of the coefficient vector $\mathbf{c}_i$ (i.e. the i_1th LCAO coefficient of orbital ψ_i).

The eigenvalues χ_i are

$$\chi_i = \langle i|Q|i\rangle = \sum_{i_1,i_2=1}^{m}\sum c_{i,i_1} c_{i,i_2} \cdot (Q^{(4)}_{i_1,i_2} + Q^{(3)}_{i_1,i_2} + Q^{(2)}_{i_1,i_2} + Q^{(1)}_{i_1,i_2}),$$

whereas the F^2 value of the Slater determinant, by comparing the formulae for Q and F^2, turns out to be

$$F^2 = 2\sum_{i=1}^{n} \sum_{i_1,i_2=1}^{m}\sum c_{i,i_1} c_{i,i_2} (\tfrac{1}{4}Q^{(4)}_{i_1,i_2} + \tfrac{1}{3}Q^{(3)}_{i_1,i_2} + \tfrac{1}{2}Q^{(2)}_{i_1,i_2} + Q^{(1)}_{i_1,i_2}) + \lambda^{*2}$$

$$= \sum_{i_1,i_2=1}^{m}\sum P_{i_1,i_2} \cdot (\tfrac{1}{4}Q^{(4)}_{i_1,i_2} + \tfrac{1}{3}Q^{(3)}_{i_1,i_2} + \tfrac{1}{2}Q^{(2)}_{i_1,i_2} + Q^{(1)}_{i_1,i_2}) + \lambda^{*2}.$$

In a subsequent paper, the iteration procedure arising from the equation deduced here will be discussed and tested by application on some simple atomic systems.

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