The Contracted Schrödinger Equation: Imposing Spin-representability Constraints upon the Correlation matrix

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Introducing Comments

The iterative solution of the Contracted Schrödinger Equation (CSE) is a recently developed method for the study of the electronic structure of atoms and molecules. In this approach,

the second-order Reduced Density Matrix

(2-RDM) is determined directly without a previous knowledge of the N-electron wave-function.

Here, a general survey of the method will be sketched.

A 2-RDM purification procedure has lately been inserted after each CSE iteration.

Attention will be centered here on the spin properties of the second-order Correlation Matrices (2-CM) which play a central role in this purification procedure.

The results of several applications for singlet states, which will be shown here, reach a precision of

10^{-5}au.

The main spin conditions for Correlation matrices corresponding to doublets and to triplets will be presented.

Some definitions

A second-order Reduced Density Matrix (2-RDM) is defined in second Quantization as:

$$^{2}D_{ij;lm} = \frac{1}{2} < \Phi| \, a_i^{\dagger} a_j^{\dagger} a_m a_l \, |\Phi >$$

In first quantization this is equivalent to the integration of the square of the N-electrons wave function over the variables of N-2 electrons.

The Matrix Contracting Mapping

Let us consider a matrix $\underline{M}$ which is the representation of an operator Θ in the N-electron space. This space is spanned by a set of N-electron configurations $|\Lambda >$. It can be shown that the contraction of this matrix into the two-electron space which is spanned by a set of two-electron configurations $|\lambda >$ is given by:

$$\sum_{\Lambda,\Omega} M_{\Lambda\Omega}\ {}^2\underline{D}^{\Lambda,\Omega} = {}^2\underline{M}$$

where the matrix ${}^2\underline{D}^{\Lambda,\Omega}$ is the second order Transition Reduced Density Matrix (2-TRDM).

That is,

$$ {}^2M_{pq;rs} = \frac{1}{2}\sum_{\Lambda,\Omega} < \Lambda|\Theta|\Omega >< \Omega|p^\dagger q^\dagger \; sr|\Lambda > $$

The contraction of the Density Matrix, D into a two-electron space is the matrix operation equivalent to the integration over N-2 electron variables

The Contracted Schrödinger Equation

The matrix representation of the Schrödinger equation is

$$\underline{\mathcal{H}}\,\underline{\mathcal{D}} = E\,\underline{\mathcal{D}}$$

The Contracted Schrödinger Equation

By applying the matrix contracting mapping (Valdemoro 1983) to both sides of this equation

$$\sum_{\Lambda,\Omega} (\mathcal{H}\mathcal{D})_{\Lambda\Omega}\ {}^{2}\underline{D}^{\Lambda,\Omega} \ = \ E\ {}^{2}\underline{D}$$

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0ne obtains the second-order CSE in a compact form

$$< \Phi|\ \hat{H}\ a_i^{\dagger} a_j^{\dagger} a_m a_l\ |\Phi > = \ E \ \ < \Phi|\ a_i^{\dagger} a_j^{\dagger} a_m a_l\ |\Phi >$$

Let us replace $\hat{H}$ by

$$\hat{H} = \frac{1}{2} \sum_{i,j,k,l} {}^{0}H_{i,j;k,l}\; a_i^{\dagger} a_j^{\dagger} a_l a_k$$

where

$${}^{0}H_{i,j;k,l} = \left[\frac{1}{N-1} (h_{i;k}\delta_{j,l} + h_{j;l}\delta_{i,k}) + < ij|kl > \right]$$

is the Reduced Hamiltonian (Bopp,Coleman, Valdemoro) which has the same symmetry properties as the two-electron matrix, The next step is to transform the left hand side of the equation

$$\frac{1}{2}\sum_{i,j,k,l} < \Phi|^0 H_{i,j;k,l}\; a_i^\dagger a_j^\dagger a_l a_k\; a_p^\dagger a_q^\dagger a_s a_r|\Phi > = \; E\; {}^2D_{pq;rs}$$

into its normal form

this matrix equation is equivalent to the integro-differential equation reported in 1976 by Cohen and Frishberg and by Nakatsuji.

Nakatsuji showed that the solution of this equation is the solution of the Schrödinger equation

The CSE is an indeterminate hierarchy equation of the form:

$$E\,{}^2\underline{D} \;=\; function(\underline{H},\; {}^2\underline{D},\; {}^3\underline{D},\; {}^4\underline{D})$$

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In a spin-orbital representation the CSE splits into three coupled equations (summations over all posible values of common indices are implicit with the restrictions $r < s$ and $k < \ell$). The $D^{\alpha\alpha}$ block, which is equivalent to the $D^{\beta\beta}$, is:

$$\underset{(i<j;p<q)}{E \;\; D^{\alpha\alpha}_{ij;pq}} = \left\{ \begin{array}{l} D^{\alpha\alpha}_{ij;rs} \; {}^{0}H^{\alpha\alpha}_{rs;pq} \\ - D^{\alpha\alpha\alpha}_{ijm;qrs} \; {}^{0}H^{\alpha\alpha}_{rs;pm} + D^{\alpha\alpha\alpha}_{ijm;prs} \; {}^{0}H^{\alpha\alpha}_{rs;qm} \\ + D^{\alpha\alpha\beta}_{ijm;puv} \; {}^{0}H^{\alpha\beta}_{uv;qm} - D^{\alpha\alpha\beta}_{ijm;quv} \; {}^{0}H^{\alpha\beta}_{uv;pm} \\ + D^{\alpha\alpha\alpha\alpha}_{ijk\ell;pqrs} \; {}^{0}H^{\alpha\alpha}_{rs;k\ell} + D^{\alpha\alpha\beta\beta}_{ijk\ell;pqrs} \; {}^{0}H^{\beta\beta}_{rs;k\ell} \\ \qquad\qquad + D^{\alpha\alpha\alpha\beta}_{ijmn;pquv} \; {}^{0}H^{\alpha\beta}_{uv;mn} \end{array} \right\}$$

And the $\alpha\beta;\alpha\beta$ block, which is the only one which is theo retically necessary for singlets, has the form:

$$E \; D^{\alpha\beta}_{ij;pq} = \left\{ \begin{array}{l} D^{\alpha\beta}_{ij;uv} \; {}^{0}H^{\alpha\beta}_{uv;pq} \\ - D^{\alpha\alpha\beta}_{mij;rsq} \; {}^{0}H^{\alpha\alpha}_{rs;pm} + D^{\alpha\beta\beta}_{ijm;prs} \; {}^{0}H^{\beta\beta}_{rs;qm} \\ - D^{\alpha\alpha\beta}_{mij;puv} \; {}^{0}H^{\alpha\beta}_{uv;mq} - D^{\alpha\beta\beta}_{ijn;uvq} \; {}^{0}H^{\alpha\beta}_{uv;pn} \\ + D^{\alpha\alpha\alpha\beta}_{k\ell ij;rspq} \; {}^{0}H^{\alpha\alpha}_{rs;k\ell} + D^{\alpha\beta\beta\beta}_{ijk\ell;pqrs} \; {}^{0}H^{\beta\beta}_{rs;k\ell} \\ \qquad + D^{\alpha\alpha\beta\beta}_{imjn;puqv} \; {}^{0}H^{\alpha\beta}_{uv;mn} \end{array} \right\}$$

where

$$\begin{aligned} {}^{0}H^{\alpha\alpha}_{rs;k\ell} &= {}^{0}H_{rs;k\ell} - {}^{0}H_{rs;\ell k} \\ {}^{0}H^{\alpha\beta}_{uv;mn} &= {}^{0}H_{u\bar{v};m\bar{n}} \\ {}^{0}H^{\beta\beta}_{rs;k\ell} &= {}^{0}H_{\bar{r}\bar{s};\bar{k}\bar{\ell}} - {}^{0}H_{\bar{r}\bar{s};\bar{\ell}\bar{k}} \end{aligned}$$

The indeterminacy of this equation can be removed by approximating the higher-order RDMs in terms of the lower-order ones (Colmenero and Valdemoro) .

It can then be solved iteratively.

The Spin-contracted Equation (SE)

Replacing the Hamiltonian by the $\hat{S}^2$ operator in the CSE one has:

$$< \Phi|\ \hat{S}^2\ a_i^\dagger a_j^\dagger a_m a_l\ |\Phi > =\ S(S+1)\ < \Phi|\ a_i^\dagger a_j^\dagger a_m a_l\ |\Phi >$$

where the spin operator is:

$$\hat{S}^2\ =\ -\sum_{r,s} a_r^\dagger\ a_{\bar{s}}^\dagger a_{\bar{r}} a_s\ +\ \left(\frac{\hat{N}_\alpha\ -\ \hat{N}_\beta}{2}\right)^2 +\ \frac{\hat{N}}{2}$$

The Spin-contracted Equation (SE)

By transforming the string of operators into its normal form in the
Spin Equation, the elements of the 2-RDM are expressed in terms of those of the 3- and 4-RDMs.
The relations thus obtained are replaced into the CSE.

This spin-adaptation of the CSE is useful in order to direct the convergence towards a stationary state of a given spin.

The iterative process consists in

- Choosing a reasonable N-representable (or closely so) 2-RDM and its corresponding 1-RDM.
- Approximating the 3- and 4-RDMs.
- Replacing all these matrices into the right-hand side of the equation, which takes the form:

$$E^{i+1}\ {}^{2}\underline{D}^{i+1} = \underline{\mathcal{M}}^{i}$$

- thus

$$E^{i+1} = \frac{tr(\underline{\mathcal{M}}^{i})}{\binom{N}{2}}$$

$${}^{2}\underline{D}^{i+1} = \frac{\underline{\mathcal{M}}^{i}}{E^{i+1}}$$

The Algorithms

for constructing high-order RDMs were obtained by extending the method proposed by Valdemoro in 1992 for approximating a 2-RDM in terms of the 1-RDM which exploited the duality between holes and particles.

In their present version, these algorithms are rather efficient.

An up-to-date revision of this subject, to which the groups of Harriman, Mazziotti, Nakatsuji and Valdemoro have actively contributed, will appear this year in Advances in Chemical Physics.
In the practice, the different proposals are rather similar. As an example, we show here the most economical algorithm for the 4-RDM:

A 4-RDM algorithm

$$
\begin{aligned}
4!\ {}^{4}D_{i,j,k,l;\,p,q,r,s} \ &= \\
\sum_{\mathcal{P}} (-1)^{\mathcal{P}}\, \mathcal{P}\ 3!\ \big(& {}^{1}D_{i;p}\ {}^{3}D_{j,k,l;q,r,s} \ + \ {}^{1}D_{j;q}\ {}^{3}D_{i,k,l;p,r,s} \\
& + {}^{1}D_{k;r}\ {}^{3}D_{i,j,l;p,q,s} \ + \ {}^{3}D_{ijk;\,p,q,r}\ {}^{1}D_{l;s} \big) \\
& - \sum_{\mathcal{P}'} (-1)^{\mathcal{P}'}\, \mathcal{P}'\ 2!\ 2!\ \big({}^{2}D_{i,j;p,q}\ {}^{2}D_{k,l;r,s} \\
& + {}^{2}D_{i,l;p,s}\ {}^{2}D_{j,k;q,r} + {}^{2}D_{i,k;p,r}\ {}^{2}D_{j,l;q,s} \big) \\
& + 4!\ {}^{4}\Delta_{i,j,k,l;p,q,r,s}
\end{aligned}
$$

A 4-RDM algorithm

$$
\begin{aligned}
4!\,{}^4D_{i,j,k,l;\,p,q,r,s} \;=\; & \\
\sum_{\mathcal{P}} (-1)^{\mathcal{P}}\,\mathcal{P}\;3!\,\big(& {}^1D_{i;p}\,{}^3D_{j,k,l;q,r,s} + {}^1D_{j;q}\,{}^3D_{i,k,l;p,r,s} \\
& + {}^1D_{k;r}\,{}^3D_{i,j,l;p,q,s} + {}^3D_{ijk;\,p,q,r}\,{}^1D_{l;s}\big) \\
& - \sum_{\mathcal{P}'} (-1)^{\mathcal{P}'}\,\mathcal{P}'\;2!\;2!\,\big({}^2D_{i,j;p,q}\,{}^2D_{k,l;r,s} \\
& + {}^2D_{i,l;p,s}\,{}^2D_{j,k;q,r} + {}^2D_{i,k;p,r}\,{}^2D_{j,l;q,s}\big) \\
& + 4!\,{}^4\Delta_{i,j,k,l;p,q,r,s}
\end{aligned}
$$

the sums on $\mathcal{P}$ and $\mathcal{P}'$ involve the permutations among the row indices of the two matrices' elements appearing in each product.

A 4-RDM algorithm

$$
\begin{aligned}
4!\ {}^4D_{i,j,k,l;\,p,q,r,s} \ &= \\
\sum_{\mathcal{P}} (-1)^{\mathcal{P}}\, \mathcal{P}\ 3!\ \big(&{}^1D_{i;p}\ {}^3D_{j,k,l;q,r,s} \ + \ {}^1D_{j;q}\ {}^3D_{i,k,l;p,r,s} \\
&+ {}^1D_{k;r}\ {}^3D_{i,j,l;p,q,s} \ + \ {}^3D_{ijk;\,p,q,r}\ {}^1D_{l;s}\big) \\
&- \sum_{\mathcal{P}'} (-1)^{\mathcal{P}'}\, \mathcal{P}'\ 2!\ 2!\ \big({}^2D_{i,j;p,q}\ {}^2D_{k,l;r,s} \\
&+ {}^2D_{i,l;p,s}\ {}^2D_{j,k;q,r} + {}^2D_{i,k;p,r}\ {}^2D_{j,l;q,s}\big) \\
&+ 4!\ {}^4\Delta_{i,j,k,l;p,q,r,s}
\end{aligned}
$$

The matrix ${}^4\Delta$ is the error of the approximation which, in Mazziotti's approach, coincides with the fourth-order cumulant of a moment expansion of the 4-RDM.

Recently, Alcoba proposed a very interesting parametric algorithm for the 4-RDM which, for given values of the parameter, yields the algorithms proposed by each of the groups working in the field. This algorithm also permits to carry out an optimization of the parameter which improves the process.

Corrections to the approximations:

- A subsidiary algorithm is used for approximating the $^3\Delta$ matrix.
- The diagonal of the 4-RDM is rendered positive semidefinite and renormalized.
- A subsidiary algorithm guaranties that the 2-, 3- and 4-RDMs are consistent among themselves with respect to contraction, while it only stores the 2- and 3-RDMs.

A Regulating Convergence Device

At present, a Convergence Regulating Device is introduced into the CSE iterative process in order to accelerate its convergence. This device consists in replacing the numerical matrix of integrals ${}^{0}\underline{H}$ by

$$
{}^{0}\underline{H}_{reg} = {}^{0}\underline{H} - \frac{A}{\binom{N}{2}} I
$$

where A is the shift of energy that one selects.

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where A is the shift of energy that one selects. The CSE takes the following form:

$$ E_{reg}\; {}^{2}\underline{D}_{reg} \;=\; \underline{M}_{reg} \;=\; \underline{M} - \; A\; {}^{2}\underline{D} $$

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$$ {}^{0}\underline{H}_{reg} = {}^{0}\underline{H} - \frac{A}{\binom{N}{2}} I $$

where A is the shift of energy that one selects. According to the choice of A, the process may be either damped or accelerated. In a CSE process an appropriate A value is:

$$ A = \frac{\binom{N}{2}}{\binom{K}{2}} Tr({}^{0}\underline{H}) $$

where K is the number of spin-orbitals.

The need for a purification procedure

When no other implementations are introduced upon the iterative process the convergence towards the FCI energy value is not complete, since the process diverges before reaching the exact value.

Mazziotti proposed to purify the 2-RDM by constraining it to obey both the D and Q N-representability conditions.

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When no other implementations are introduced upon the iterative process the convergence towards the FCI energy value is not complete, since the process diverges before reaching the exact value.

Mazziotti proposed to purify the 2-RDM by constraining it to obey both the D and Q N-representability conditions. He inserted this purification procedure after each CSE iteration; and the convergence of the overall process was significantly improved. This clearly indicated that the 2-RDM should be rendered as closely N-representable as possible.

Our approach to the purification procedure

Since

$$2!\,{}^{2}D_{i,j;k,l} \;=\; {}^{1}D_{i;k}\,{}^{1}D_{j;l} \;-\; \delta_{k,j}\,{}^{1}D_{i;l} + \;\mathcal{C}_{i,j;k,l}\;,$$

the part of the 2-RDM which causes problems is the

Correlation matrix C.

Thus, the emphasis should be set on correcting this matrix.

The form of the Correlation matrix is

$$\mathcal{C}_{i,j;k,l} = \sum_{\Phi' \neq \Phi} < \Phi|\, a_i^\dagger\, a_k\, |\Phi' >< \Phi'|\, a_j^\dagger a_l\, |\Phi >$$

The CM is directly related to the Garrod and Percus G-matrix

$$\mathcal{C}_{i,j;k,l} = G_{i,k;l,j}$$

And representing just the spins of the different states

$$\begin{aligned}\mathcal{C}_{\sigma\sigma';\tau\tau'} &= \sum (S,M|\,\sigma^\dagger\,\tau\,|S',M')(S',M'|\sigma'^\dagger\tau'\,|S,M) \\ &= \;G_{\sigma\tau;\tau'\sigma'}\end{aligned}$$

Clearly, C and G have a set of spin-components.

In what follows the analysis will be centered on the G-matrix because

$$\underline{G} \ \underline{\geq} \ 0$$

and this property must reflect the properties of the G spin-components. Thus,

In a 2-RDM purification procedure–besides the D and Q-conditions –the properties of the G spin-components should also be imposed.

Spin properties of the G-matrices

The set of conditions that the spin-components of the CM or, equivalently, the G-matrix must satisfy when corresponding to a pure spin-state were reported last year in International Journal of Quantum Chemistry.

Here we will consider the form taken by these general relations in the three specific cases:

SINGLET, DOUBLET and TRIPLET

The Singlet case

In what follows, a bar over an index indicates a β spin-orbital. The decomposition of the G-matrix in terms of the spin components is:

$$\begin{aligned}
G_{i,k;l,j} &= {}_{(0,0)}G_{i,k;l,j} + {}_{(1,0)}G_{i,k;l,j} \\
G_{i,\bar{k};l,\bar{j}} &= {}_{(1,-1)}G_{i,\bar{k};l,\bar{j}} \\
G_{i,k;\bar{l},\bar{j}} &= {}_{(0,0)}G_{i,k;\bar{l}\bar{j}} + {}_{(1,0)}G_{i,k;\bar{l};\bar{j}}
\end{aligned}$$

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G_{i,k;\bar{l},\bar{j}} &= {}_{(0,0)}G_{i,k;\bar{l}\bar{j}} + {}_{(1,0)}G_{i,k;\bar{l};\bar{j}}
\end{aligned}
$$

The symbols $(0,0)$, $(1,0)$, $(1,-1)$ refer to the (S',M') quantum numbers of the Φ' states in

$$G_{i,k;l,j} = \sum_{\Phi' \neq \Phi} < \Phi|\; a_i^\dagger\; a_k\; |\Phi' >< \Phi'|\; a_j^\dagger;\, a_l\; |\Phi >$$

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G_{i,k;\bar{l},\bar{j}} &= {}_{(0,0)}G_{i,k;\bar{l}\bar{j}} + {}_{(1,0)}G_{i,k;\bar{l};\bar{j}}
\end{aligned}$$

The other relevant relations are:

$$\begin{aligned}
G_{i,\bar{k};l,\bar{j}} &= -2\ {}_{(1.0)}G_{i,k;\bar{l},\bar{j}} \\
G_{i,\bar{l};k,\bar{j}} &= {}^{1}D_{i;k}\,\delta_{j;l} - {}^{1}D_{i;k}\,{}^{1}D_{\bar{j};\bar{l}} - G_{i,k;\bar{l}\bar{j}}
\end{aligned}$$

Thus, only the block-matrix $G_{\alpha\beta;\alpha,\beta}$ is needed to get all the spin-components.

The two following needed conditions are:

$$ {}_{(0,0)}G_{\alpha,\alpha;\alpha,\alpha} \geq 0 $$

$$ {}_{(1,-1)}G_{\alpha,\beta;\alpha,\beta} \geq 0 $$

The D and Q conditions are also imposed in our purification procedure.

The Doublet case

When the state is a doublet with $M = \frac{1}{2}$, the relations linking the different spin components of the G-matrix are:

$$
{}_{(\frac{1}{2},-\frac{1}{2})}G_{i,\bar{l};m,\bar{j}} = \left(\begin{array}{l} + {}_{(\frac{1}{2},\frac{1}{2})}G_{i,l;m,j} + {}_{(\frac{1}{2},\frac{1}{2})}G_{\bar{i},\bar{l};\bar{m},\bar{j}} \\ - {}_{(\frac{1}{2},\frac{1}{2})}G_{i,l;\bar{m},\bar{j}} - {}_{(\frac{1}{2},\frac{1}{2})}G_{\bar{i},\bar{l};m,j} \\ +({}^1D_{i;l} - {}^1D_{\bar{i};\bar{l}})({}^1D_{m;j} - {}^1D_{\bar{m};\bar{j}}) \end{array} \right)
$$

$$
\begin{aligned}
\frac{1}{3}\, G_{\bar{i},l;\bar{m},j} &= \frac{1}{3}\, {}_{(\frac{3}{2},\frac{3}{2})}G_{\bar{i},l;\bar{m},j} = {}_{(\frac{3}{2},-\frac{1}{2})}G_{i,\bar{l};m,\bar{j}} \\
&= {}_{(\frac{3}{2},\frac{1}{2})}G_{i,l;m,j} = {}_{(\frac{3}{2},\frac{1}{2})}G_{\bar{i},\bar{l};\bar{m},\bar{j}} \\
&= -\, {}_{(\frac{3}{2},\frac{1}{2})}G_{\bar{i},\bar{l};m,j} = -\, {}_{(\frac{3}{2},\frac{1}{2})}G_{i,l;\bar{m},\bar{j}}
\end{aligned}
$$

Besides the D and Q N-representability conditions, the purification code for doublets which is now in progress imposes:

$$
\begin{aligned}
{}^{(\frac{1}{2},-\frac{1}{2})}G_{\alpha\beta;\alpha\beta} &\geq 0 \\
{}^{(\frac{3}{2},\frac{3}{2})}G_{\beta\alpha;\beta\alpha} &\geq 0 \\
{}^{(\frac{1}{2},-\frac{1}{2})}\underline{G} &\geq 0
\end{aligned}
$$

The Triplet case

For a triplet state with $M = 1$, the relations linking the different spin-components of the G-matrix are:

$$2\ {}_{(1,0)}G_{i,\bar{l};m,\bar{j}} = \begin{pmatrix} +\ {}_{(1,1)}G_{i,l;m,j} + {}_{(1,1)}G_{\bar{i},\bar{l};\bar{m},\bar{j}} \\ -\ {}_{(1,1)}G_{i,l;\bar{m},\bar{j}} - {}_{(1,1)}G_{\bar{i},\bar{l};m,j} \\ +({}^1D_{i;l} -{}^1 D_{\bar{i};\bar{l}})({}^1D_{m;j} -{}^1 D_{\bar{m};\bar{j}}) \end{pmatrix}$$

$$\begin{aligned} \frac{1}{4}\, G_{\bar{i},l;\bar{m},j} \equiv \frac{1}{4}\ {}_{(2,2)}G_{\bar{i},l;\bar{m},j} &= \frac{3}{2}\ {}_{(2,0)}G_{i,\bar{l};m,\bar{j}} \\ &= {}_{(2,1)}G_{\bar{i},\bar{l};\bar{m},\bar{j}} = {}_{(2,1)}G_{i,l;m,j} \\ &= -\ {}_{(2,1)}G_{i,l;\bar{m},\bar{j}} = -\ {}_{(2,1)}G_{\bar{i},\bar{l};m,j} \end{aligned}$$

By using the G matrix spin-blocks all its spin-components can be obtained. The spin-conditions which must be imposed are:

$$ {}^{(1,0)}G_{\alpha\beta;\alpha\beta} \geq 0 $$

$$ {}^{(2,2)}G_{\beta\alpha;\beta\alpha} \geq 0 $$

$$ {}^{(0,0)}G_{\alpha\beta;\alpha\beta} \geq 0 $$

$$ {}^{(1,1)}\underline{G} \geq 0 $$

Vanishing Sums

Besides the positivity of the G-matrix blocks there are other conditions that these matrices must satisfy. Thus, in singlets one has:

$$\sum_{m}^{K} \sum_{\Phi'\neq\Phi} \langle\Phi| \underbrace{a_m^\dagger \, a_{\bar{m}}} |\Phi'\rangle \, \langle\Phi'| \, a_{\bar{l}}^\dagger \, a_i \, |\Phi\rangle = \sum_{m}^{K} G_{\underbrace{m\bar{m}};\, i\bar{l}} = 0$$

For doublets and triplets more vanishing sums must be imposed during the purification procedure.
These vanishing sums derive from the properties of the operators $\hat{S}_+$, or $\hat{S}_-$, or $\hat{N}$, and the orthogonality of the eigenstates involved.

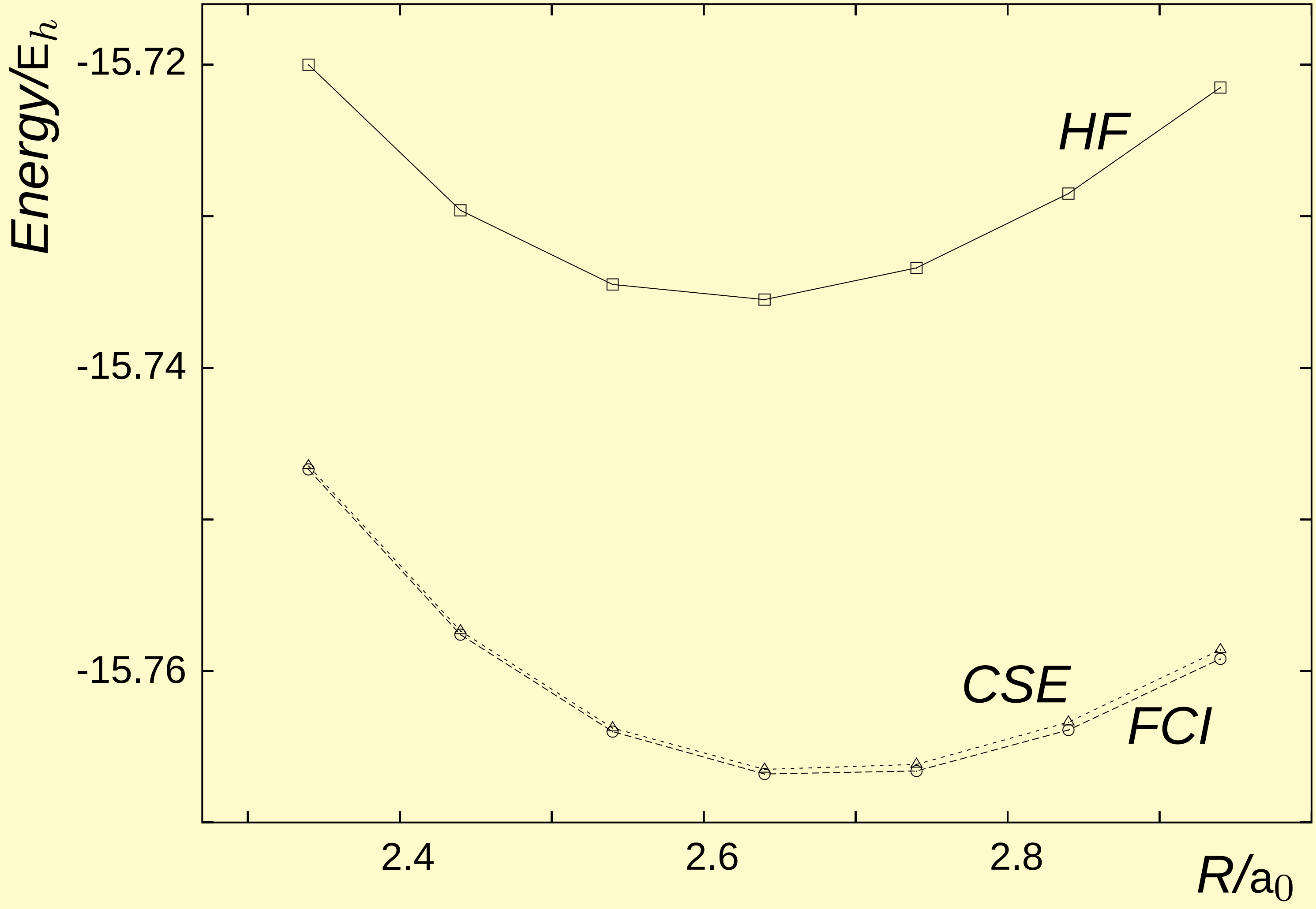
Some Singlet Results

The results obtained in the calculation of the potential energy curves for the symmetric bond stretchings of

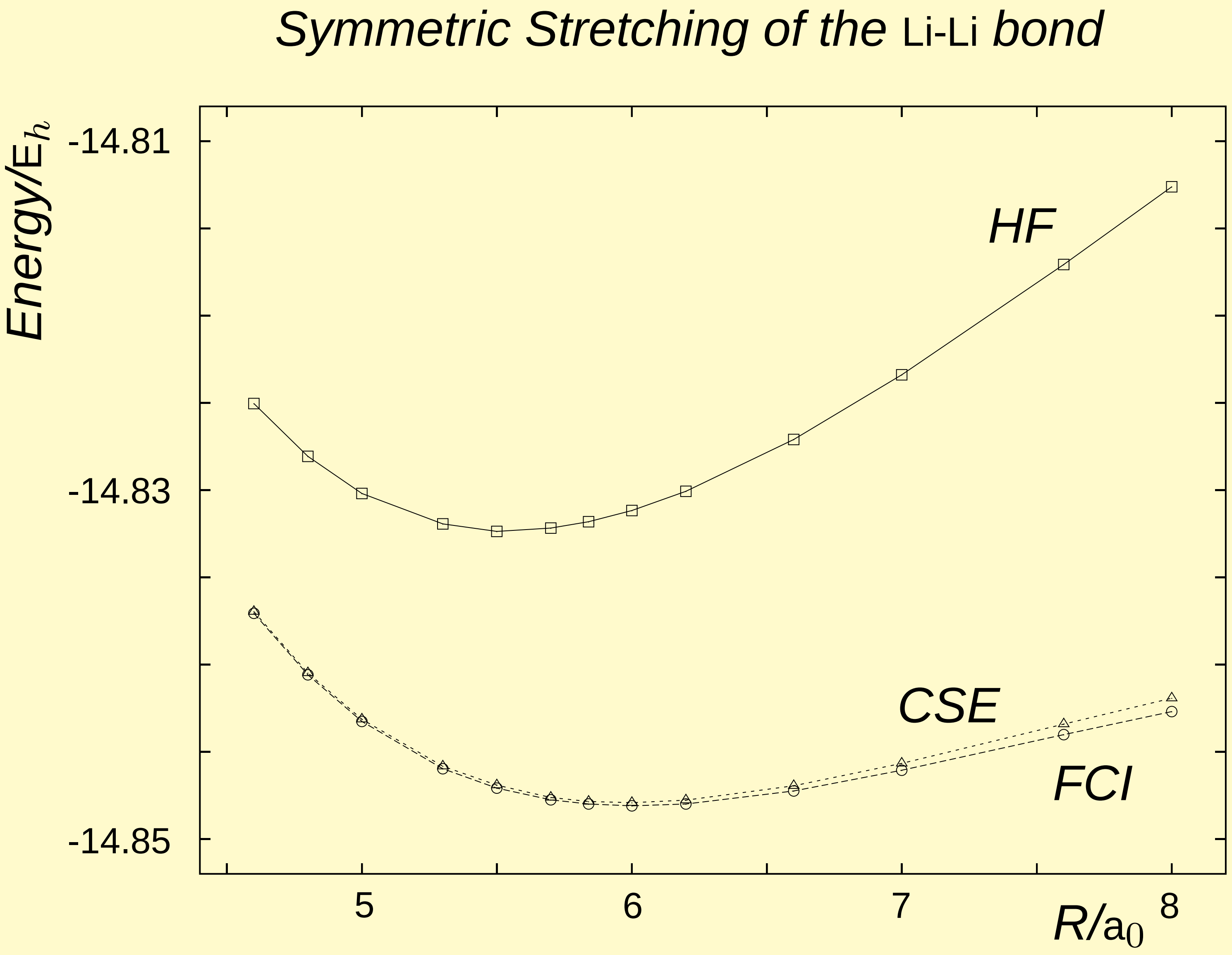
BeH_2 and Li_2

will now be presented.

Symmetric Stretching of the H-Be-H *bond*



Some results



BeH$_2$

Performance of the purification procedure

	Without	(15 Iterations)	(35 Iterations)
D	$-1.79\ 10^{-4}$	$-1.06\ 10^{-5}$	$-6.42\ 10^{-6}$
Q	$-6.89\ 10^{-4}$	$-1.99\ 10^{-5}$	$-1.10\ 10^{-5}$
G	$-1.32\ 10^{-3}$	$-2.02\ 10^{-5}$	$-1.35\ 10^{-5}$
Δ E	-0.0018	$+0.0006$	$+0.0006$

	(55 Iterations)
D	$-4.31\ 10^{-6}$
Q	$-3.92\ 10^{-6}$
G	$-1.22\ 10^{-5}$
Δ E	$+0.0006$

Li_2

Performance of the purification procedure

	Without	(15 Iterations)	(35 Iterations)
D	-1.90 x 10^{-4}	7.04 x 10^{-6}	2.91 x 10^{-7}
Q	-3.86 x 10^{-3}	-3.08x 10^{-5}	-2.05 x 10^{-5}
G	-1.73 x 10^{-3}	-7.55 x 10^{-6}	-5.30 x 10^{-6}
△ E	$+0.0070$	$+0.0001$	$+0.0001$

	(55 Iterations)
D	3.56 x 10^{-8}
Q	-1.62 x 10^{-5}
G	-4.22 x 10^{-6}
△ E	$+0.0001$

These results were obtained with $40/100$ CSE iterations for BeH_2/Li_2.When more iterations were carried out the precision reached at the equilibrium point was of 10^{-5}au. in both cases.

As shown, the purification procedure imposing the

$$D, \quad Q, \quad {}_{(S',M')}G \quad \text{conditions}$$

in the SINGLET case yielded very good applicative results.

Concluding Remarks

The iterative solution of the spin-adapted CSE for Singlets can now be considered a

COMPETITIVE METHOD

to the study of the electronic structure of atoms and molecules.

Concluding Remarks

This is mainly due to the
conditions imposed on the G spin-components
through our 2-RDM purification procedure
at each CSE iteration.

Concluding Remarks

In spite of the higher complexity of these cases, a similar good performance can be expected for the

DOUBLETS AND TRIPLETS

purification procedures.

Programming codes

- At present the purification code for the Doublet states is being developped and after this is achieved the code for Triplets will be written.
- The memory and execution time of the present codes should be optimized by computing experts in order to render them as *black boxes* as the *Gaussian, Gamess,etc* ones.

Work in progress

Theoretical Research in progress

- The states whose first-order description needs more than one determinant is still an open question since in those cases the 3-RDM and 4-RDM cumulant matrices have rather large valued elements. Approximations for these elements are being looked for.
- We are considering different possible approaches in order to apply the CSE methodology to the calculation of large systems. We expect that the philosophy "*Dividing to vanquish*" jointly with the theoretical developments of Alcoba, Bochicchio,Laín and Torre for *Open systems* Reduced Density Matrices may render this possible.