Exploiting non-Abelian symmetry in AO-driven CIS, RPA, and TDDFT calculations

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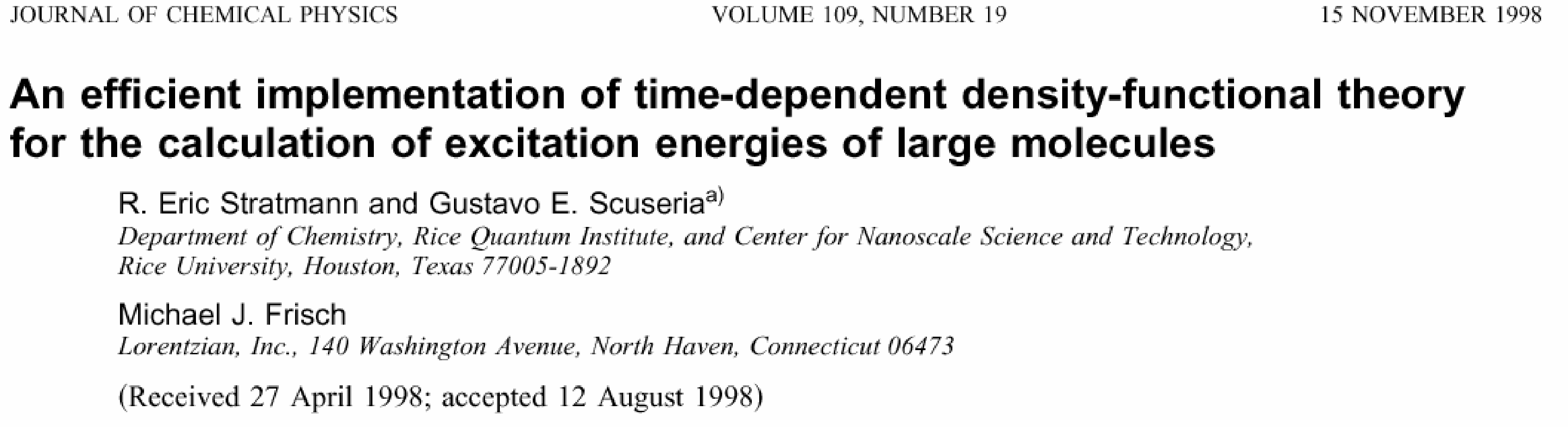

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An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules

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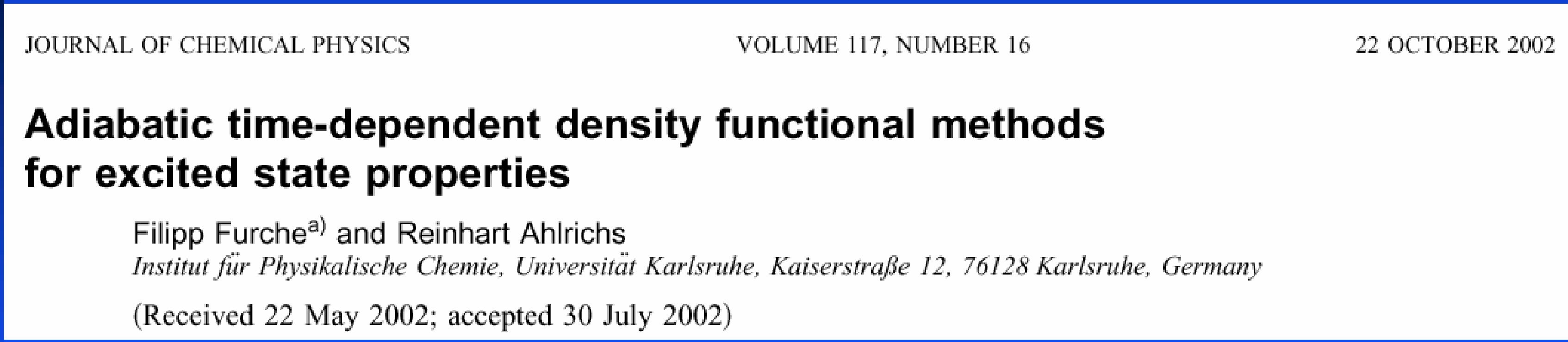

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Adiabatic time-dependent density functional methods for excited state properties

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RPA & TDDFT master equation

The basic statement is that excitation energies are the stationary points of the functional

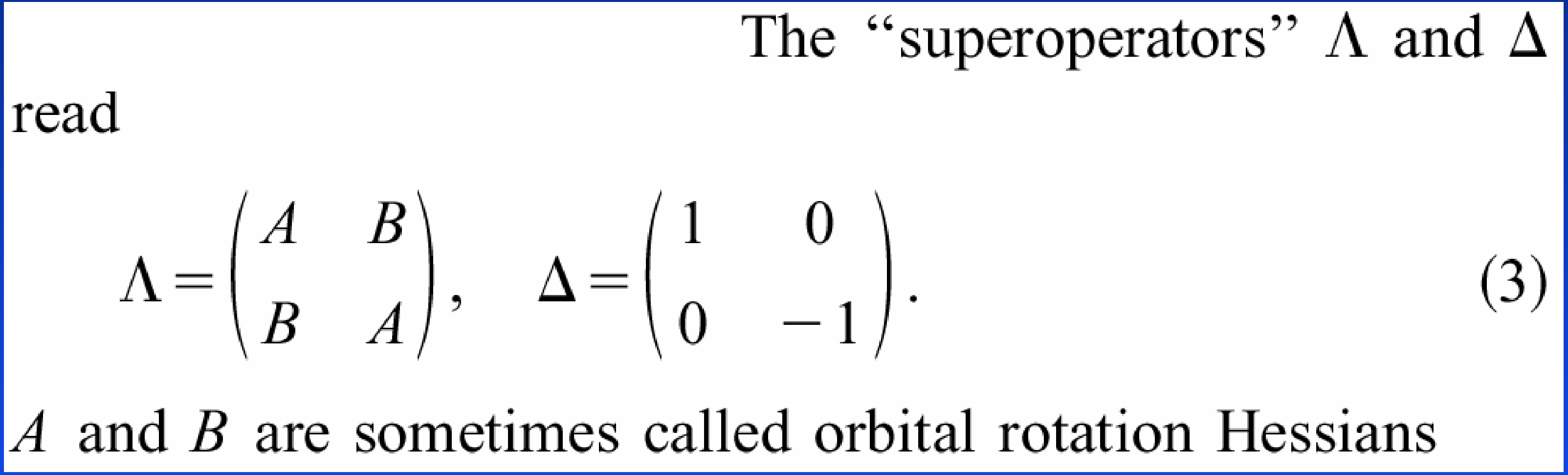
$$G[X,Y,\Omega]=\langle X,Y|\Lambda|X,Y\rangle-\Omega(\langle X,Y|\Delta|X,Y\rangle-1). \quad (1)$$

Ω is a real Lagrange multiplier, and the vectors

$$|X,Y\rangle=\begin{pmatrix} X \\ Y \end{pmatrix} \quad (2)$$

are defined on the Hilbert space $L=L_{\text{virt}}\times L_{\text{occ}}\oplus L_{\text{occ}}\times L_{\text{virt}}$, where L_{occ} and L_{virt} denote the Hilbert spaces of occupied (occ) and virtual (virt) molecular orbitals (MOs), respectively. The MOs $\varphi_{p\sigma}(\mathbf{r})$ are solutions of the static KS equations with eigenvalues $\epsilon_{p\sigma}$. As usual, indices $i,j,\ldots$ label occupied, $a,b,\ldots$ virtual, and $p,q,\ldots$ general MOs. We assume the MOs to be real, which is always possible in the absence of magnetic fields.

RPA & TDDFT master equation



The "superoperators" Λ and Δ read

$$\Lambda = \begin{pmatrix} A & B \\ B & A \end{pmatrix}, \quad \Delta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{3}$$

A and B are sometimes called orbital rotation Hessians

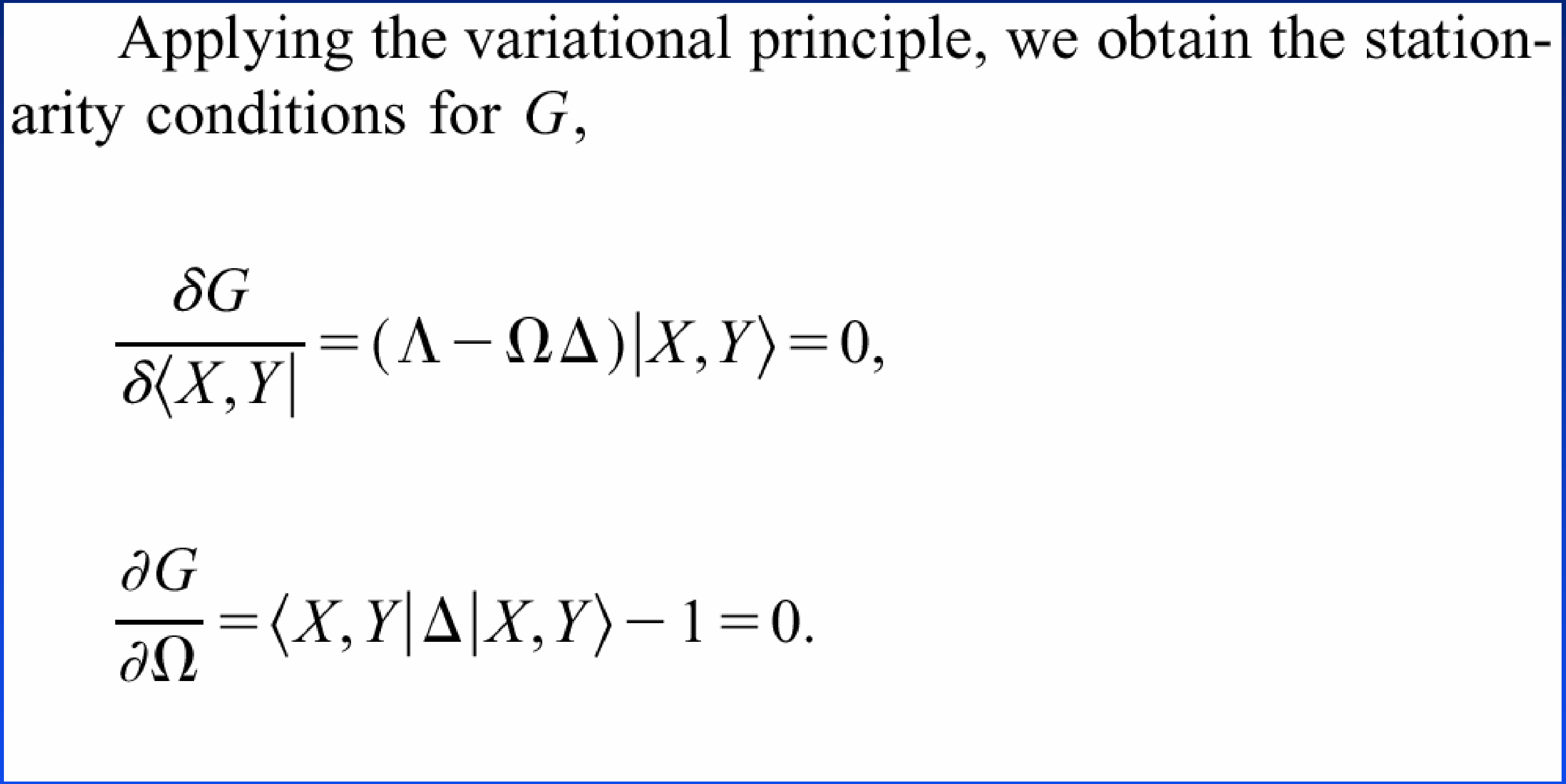
A and B matrices

$$
\begin{aligned}
(A+B)_{ia\sigma jb\sigma'} = {} & (\epsilon_{a\sigma} - \epsilon_{i\sigma})\,\delta_{ij}\delta_{ab}\delta_{\sigma\sigma'} \\
& + 2(ia\sigma|jb\sigma') + 2 f^{\mathrm{xc}}_{ia\sigma jb\sigma'} \\
& - c_{\mathrm{x}}\delta_{\sigma\sigma'}[(ja\sigma|ib\sigma) + (ab\sigma|ij\sigma)], \\
(A-B)_{ia\sigma jb\sigma'} = {} & (\epsilon_{a\sigma} - \epsilon_{i\sigma})\,\delta_{ij}\delta_{ab}\delta_{\sigma\sigma'} + c_{\mathrm{x}}\delta_{\sigma\sigma'}[(ja\sigma|ib\sigma) \\
& - (ab\sigma|ij\sigma)].
\end{aligned}
$$

$(pq\sigma|rs\sigma')$ is a two-electron repulsion integral in Mulliken notation, and $f^{\mathrm{xc}}_{pq\sigma rs\sigma'}$ represents a matrix element of the exchange-correlation kernel in the adiabatic approximation,

$$
f^{\mathrm{xc}}_{\sigma\sigma'}(\mathbf{r},\mathbf{r}') = \frac{\delta^2 E^{\mathrm{xc}}}{\delta\rho_\sigma(\mathbf{r})\,\delta\rho_{\sigma'}(\mathbf{r}')}.
$$

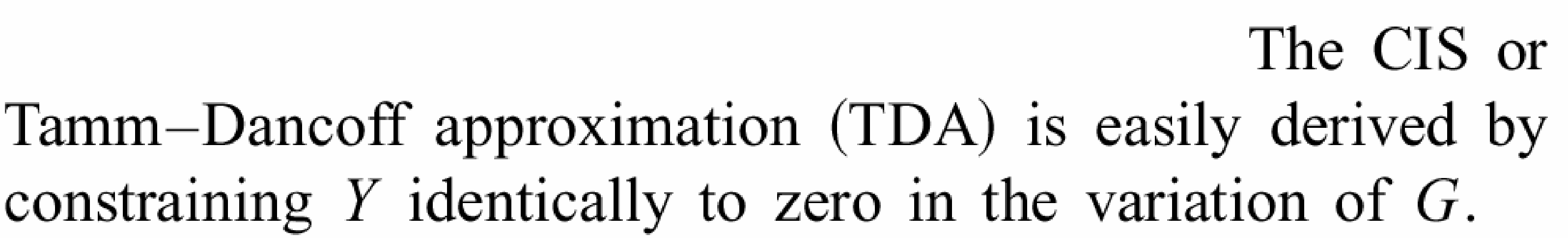
RPA & TDDFT master equation



Applying the variational principle, we obtain the stationarity conditions for G,

$$\frac{\delta G}{\delta \langle X, Y|} = (\Lambda - \Omega \Delta)|X, Y\rangle = 0,$$

$$\frac{\partial G}{\partial \Omega} = \langle X, Y|\Delta|X, Y\rangle - 1 = 0.$$



The CIS or Tamm–Dancoff approximation (TDA) is easily derived by constraining Y identically to zero in the variation of G.

How to solve?

- CIS
  - Davidson diagonalization
    - Requires construction of **A·X** products for trial vectors X
- RPA & TDDFT
  - Davidson-like diagonalization methods
    - Require construction of **(A+B)·X, (A+B)·Y, (A-B)·X, (A-B)·Y** products for trial vectors X and Y
- <u>For our purposes, it is sufficient to consider in details CIS only</u>.

AO-driven CIS

- Let us consider RHF-based CIS for simplicity
- Let us transform basis from determinants to SAPS (CSF) to solve separate problems for singlet states (and triplet states) and to avoid spin-orbitals.
- $\mathbf{A\cdot X = \Sigma_{jb}A_{ia,jb}\cdot X_{jb}}$
  - $\mathbf{A_{ia,jb}}=(\varepsilon_a - \varepsilon_i)\delta_{ij}\,\delta_{ab} + \ldots$
    - The most efficient way to evaluate this part of the matrix-vector product is to use MO basis.
  - $\mathbf{A_{ia,jb}}=\ldots + (ia|jb) +$ exchange-related terms
    - The most efficient way to calculate these parts of matrix-vector product (most time-consuming step) is to use AO basis:
    - $\mathbf{\Sigma_{jb}(ia|jb)\cdot X_{jb} = \Sigma_{jb}\,\Sigma_{pqrs}C_{ip}C_{aq}C_{jr}C_{bs}\,(pq|rs)\cdot X_{jb} = \Sigma_{pq}C_{ip}C_{aq}\Sigma_{rs}\,(pq|rs)\cdot(\Sigma_{jb}C_{jr}C_{bs}X_{jb})}$

AO-driven CIS benefits

- Does not require integral transformation
  - applicable to very large systems
  - simplifies use of molecular symmetry
- Is based on the construction of Fock-like matrices
  - All known approaches used to solve large-scale SCF problems can be also used in the case of CIS
    - Linear scaling
      - QFMM
      - Linear exchange

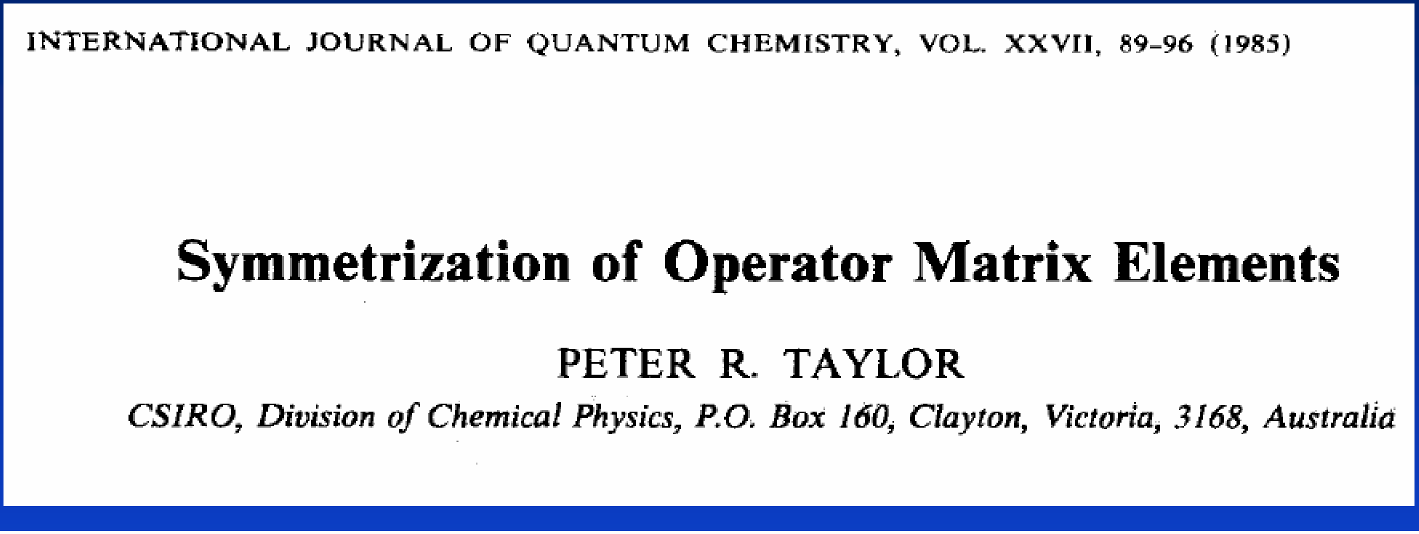
Main CIS and SCF differences

- CIS operates with non-symmetrical (square) density-like and Fock-like matrices
- CIS results in non totally-symmetric density and Fock-like matrices. The symmetry is defined by the symmetry of the target CIS state

Reminiscence. Use of molecular point group symmetry in SCF methods

- At least two different ways:
  - Use of symmetrized AO basis functions and 2-e integrals
  - <u>Use of petite AO integral list:</u>
    - Construction of the skeleton Fock matrix
    - Projection/symmetrization to the totally symmetric irreducible representation at the end

Skeleton matrix symmetrization



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Symmetrization of Operator Matrix Elements

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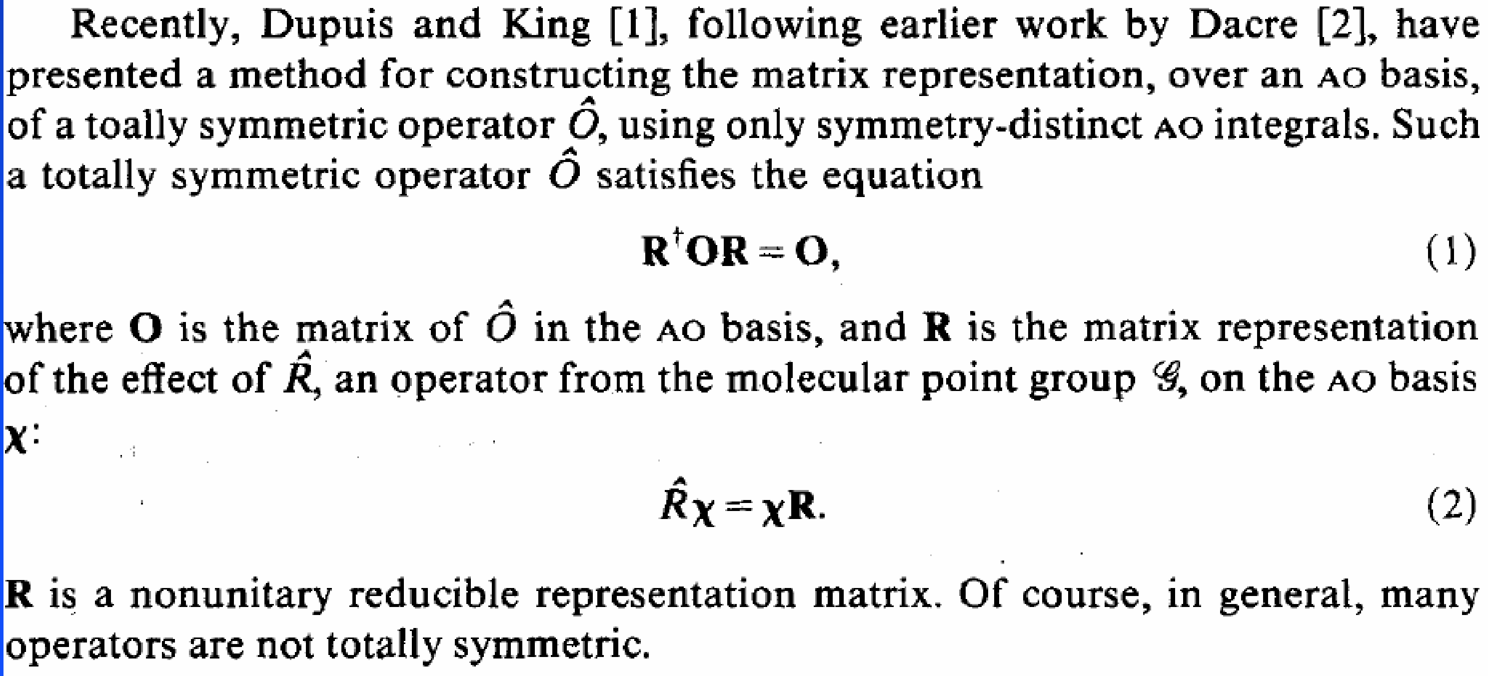


Recently, Dupuis and King [1], following earlier work by Dacre [2], have presented a method for constructing the matrix representation, over an AO basis, of a toally symmetric operator $\hat{O}$, using only symmetry-distinct AO integrals. Such a totally symmetric operator $\hat{O}$ satisfies the equation

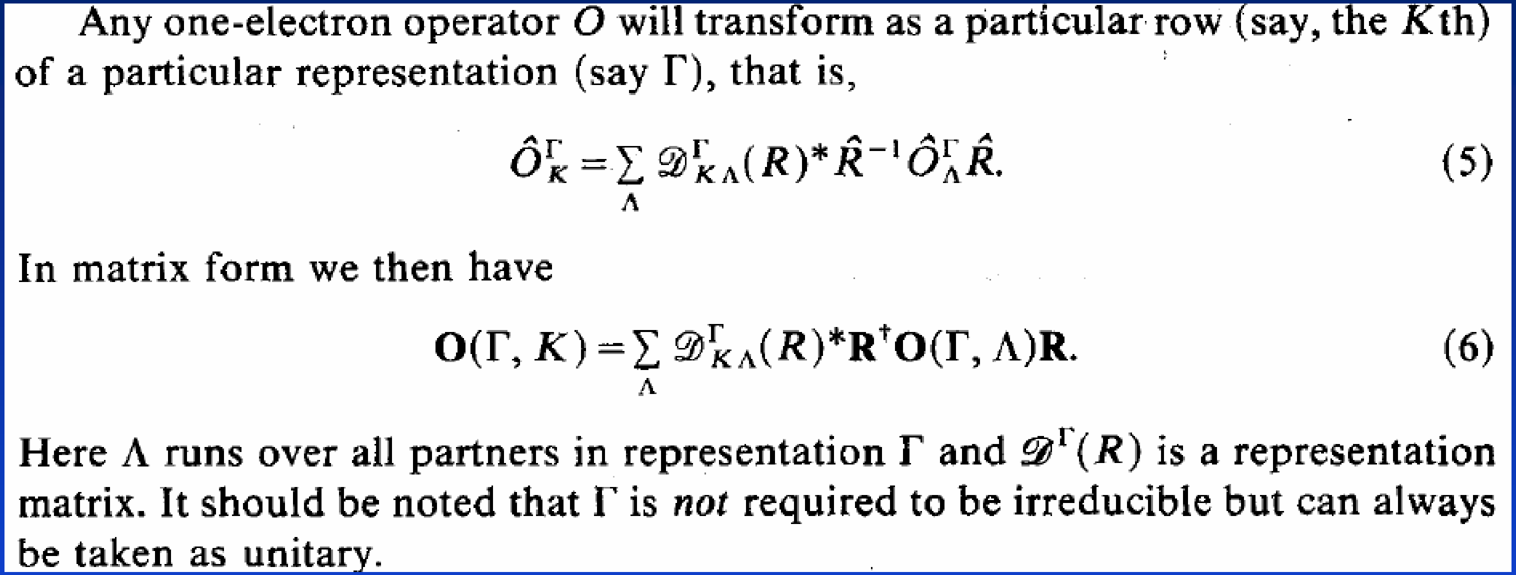
$$\mathbf{R}^{\dagger}\mathbf{O}\mathbf{R} = \mathbf{O}, \tag{1}$$

where $\mathbf{O}$ is the matrix of $\hat{O}$ in the AO basis, and $\mathbf{R}$ is the matrix representation of the effect of $\hat{R}$, an operator from the molecular point group $\mathscr{G}$, on the AO basis $\boldsymbol{\chi}$:

$$\hat{R}\chi = \chi\mathbf{R}. \tag{2}$$

$\mathbf{R}$ is a nonunitary reducible representation matrix. Of course, in general, many operators are not totally symmetric.

Skeleton matrix symmetrization



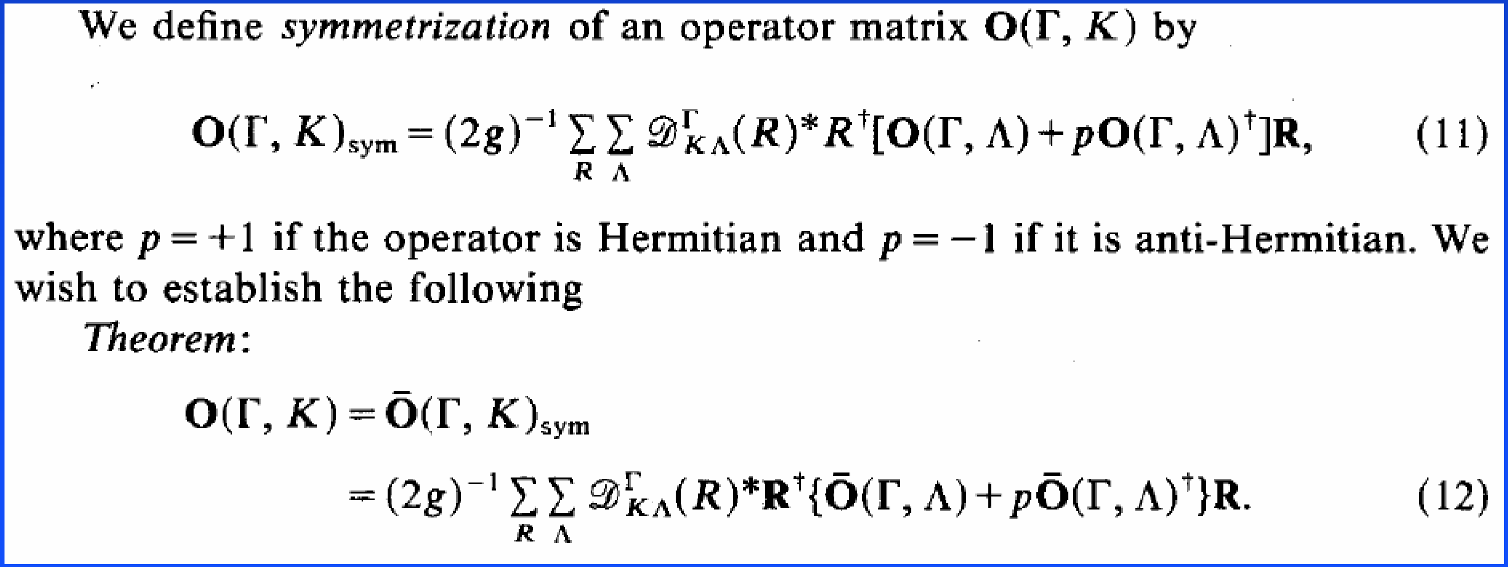
Any one-electron operator O will transform as a particular row (say, the Kth) of a particular representation (say Γ), that is,

$$\hat{O}^{\Gamma}_{K} = \sum_{\Lambda} \mathscr{D}^{\Gamma}_{K\Lambda}(R)^{*}\hat{R}^{-1}\hat{O}^{\Gamma}_{\Lambda}\hat{R}. \tag{5}$$

In matrix form we then have

$$\mathbf{O}(\Gamma, K) = \sum_{\Lambda} \mathscr{D}^{\Gamma}_{K\Lambda}(R)^{*}\mathbf{R}^{\dagger}\mathbf{O}(\Gamma, \Lambda)\mathbf{R}. \tag{6}$$

Here Λ runs over all partners in representation Γ and $\mathscr{D}^{\Gamma}(R)$ is a representation matrix. It should be noted that Γ is *not* required to be irreducible but can always be taken as unitary.



We define *symmetrization* of an operator matrix $\mathbf{O}(\Gamma, K)$ by

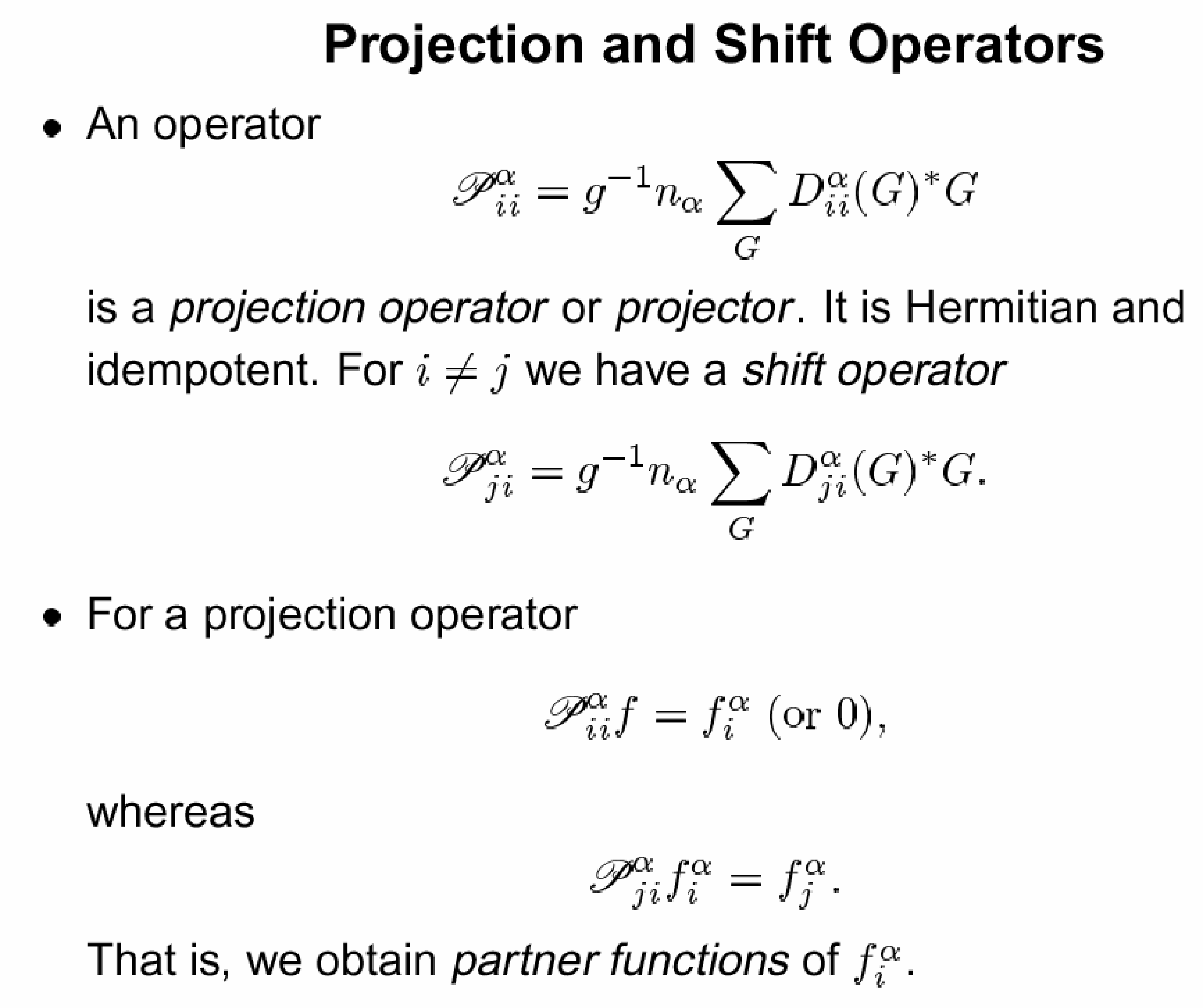
$$\mathbf{O}(\Gamma, K)_{\text{sym}} = (2g)^{-1}\sum_{R}\sum_{\Lambda} \mathscr{D}^{\Gamma}_{K\Lambda}(R)^{*}R^{\dagger}[\mathbf{O}(\Gamma, \Lambda) + p\mathbf{O}(\Gamma, \Lambda)^{\dagger}]\mathbf{R}, \tag{11}$$

where $p = +1$ if the operator is Hermitian and $p = -1$ if it is anti-Hermitian. We wish to establish the following

Theorem:

$$\begin{aligned}\mathbf{O}(\Gamma, K) &= \bar{\mathbf{O}}(\Gamma, K)_{\text{sym}}\\ &= (2g)^{-1}\sum_{R}\sum_{\Lambda} \mathscr{D}^{\Gamma}_{K\Lambda}(R)^{*}\mathbf{R}^{\dagger}\{\bar{\mathbf{O}}(\Gamma, \Lambda) + p\bar{\mathbf{O}}(\Gamma, \Lambda)^{\dagger}\}\mathbf{R}. \qquad (12)\end{aligned}$$

Terminology



Projection and Shift Operators

- An operator

$$\mathscr{P}^{\alpha}_{ii} = g^{-1} n_{\alpha} \sum_{G} D^{\alpha}_{ii}(G)^{*} G$$

is a *projection operator* or *projector*. It is Hermitian and idempotent. For $i \neq j$ we have a *shift operator*

$$\mathscr{P}^{\alpha}_{ji} = g^{-1} n_{\alpha} \sum_{G} D^{\alpha}_{ji}(G)^{*} G.$$

- For a projection operator

$$\mathscr{P}^{\alpha}_{ii} f = f^{\alpha}_{i} \ (\text{or } 0),$$

whereas

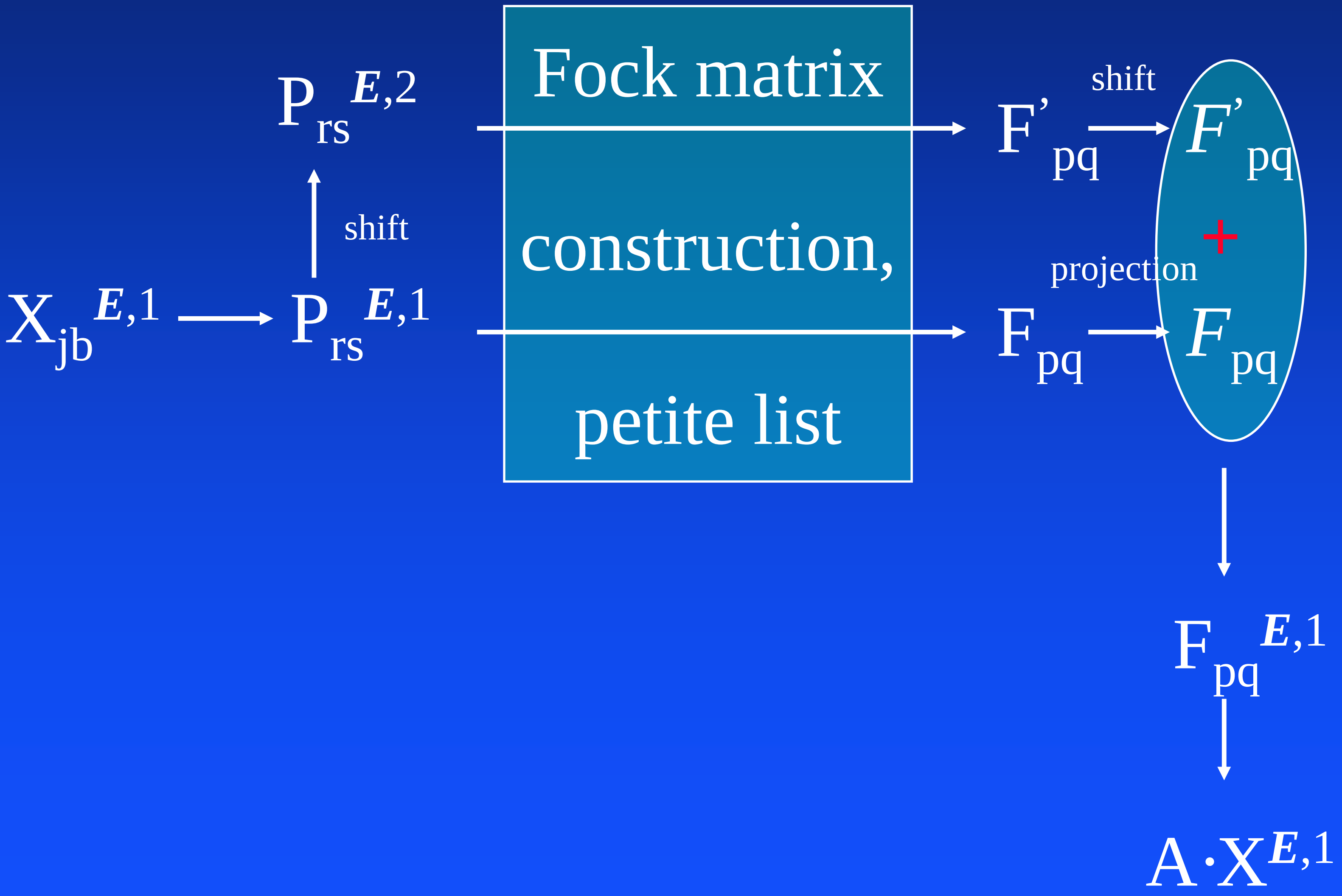
$$\mathscr{P}^{\alpha}_{ji} f^{\alpha}_{i} = f^{\alpha}_{j}.$$

That is, we obtain *partner functions* of f^{α}_{i}.

Gathering things together

- Now we have all the tools to construct algorithm for (any symmetry) Fock-like matrix assembly using petite integral list
- Let us consider some 2-d irrep. ***E*** without the loss of generality.
- We are interested in getting CIS states transforming, say, as the first row of ***E*** only, as their counterparts can be constructed (if needed at all) after diagonalization of the CIS Hamiltonian using shift operators.

Strategy



$P_{rs}^{\boldsymbol{E},2}$

shift

$X_{jb}^{\boldsymbol{E},1} \longrightarrow P_{rs}^{\boldsymbol{E},1}$

Fock matrix construction, petite list

$F'_{pq} \xrightarrow{\text{shift}} F'_{pq}$

$+$

$F_{pq} \xrightarrow{\text{projection}} F_{pq}$

$F_{pq}^{\boldsymbol{E},1}$

$A \cdot X^{\boldsymbol{E},1}$

The only nontrivial (?) point

- Shift and projection operators for density-like matrices are not the same as for Fock-like matrices!
  - Fock-like matrices:
    - $\mathbf{R}(g)$
  - Density-like matrices:
    - $\mathbf{R}(g)$ should be replaced by $\mathbf{R}^{+}(g^{-1})$

Thank you for your attention!