Requiem for MCQDPT: the Dawn of XMCQDPT Theory

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MCQDPT2 in Firefly: status

- Very efficient state of the art implementation is available
  - **Capable to handle up to several thousands basis functions with active spaces up to several millions CSFs**
  - **Details are described in two presentations on the PC GAMESS/Firefly homepage**

MCQDPT2 in Firefly: applications

- Huge amount of data for different **large** systems obtained as the result of our activity
  - **Deep insight and huge experience**
  - **Huge statistics**

MCQDPT2: immanent problems

- Off-diagonal elements of H_{eff} seems to be ***randomly*** overestimated by up to two orders of magnitude
  - *Especially pertained for large systems*
  - *Especially pertained if common set of leading CSFs is spanned by the reference MCSCF wavefunctions*
- Within MCQDPT2, H_{eff} does not explicitly depend on the model space dimension (***N***)
  - *H^{N}_{eff} is simply enclosed into H^{N+1}_{eff}, etc…*
  - *The diagonal elements of H_{eff} are just the (state-averaged) approximations to the (state-specific) MR-MP2 energies*
    - *Do then off-diagonal elements have any sense at all???*

MCQDPT2 failure: an example

All-trans Retinal protonated Shiff base molecule

cc-pVTZ basis set

1445 Cartesian AOs, CAS(12,12)

S_0-S_1 transition

Double excitations from double occupied to virtual orbitals are taken into account using MP2-like formulas to **decrease** off-diagonal elements of effective Hamiltonian

```
############################
###   MC-QDPT2 RESULTS   ###
############################
*** EFFECTIVE HAMILTONIAN (0-2) ***
-----------------------------------
                  1            2
    1 -9.897411D+02
    2 -2.973794D-02-9.896678D+02
```

S_0-S_1 transition energy:

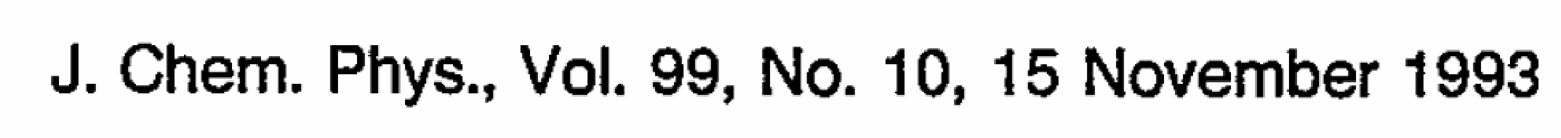
- **Experiment: 620-640 nm**
- **Using diagonal elements of H_{eff} (MR-MP2 like): 622 nm**
- **From H_{eff} diagonalization: 483 nm**

MCQDPT2: “experimental” conclusion

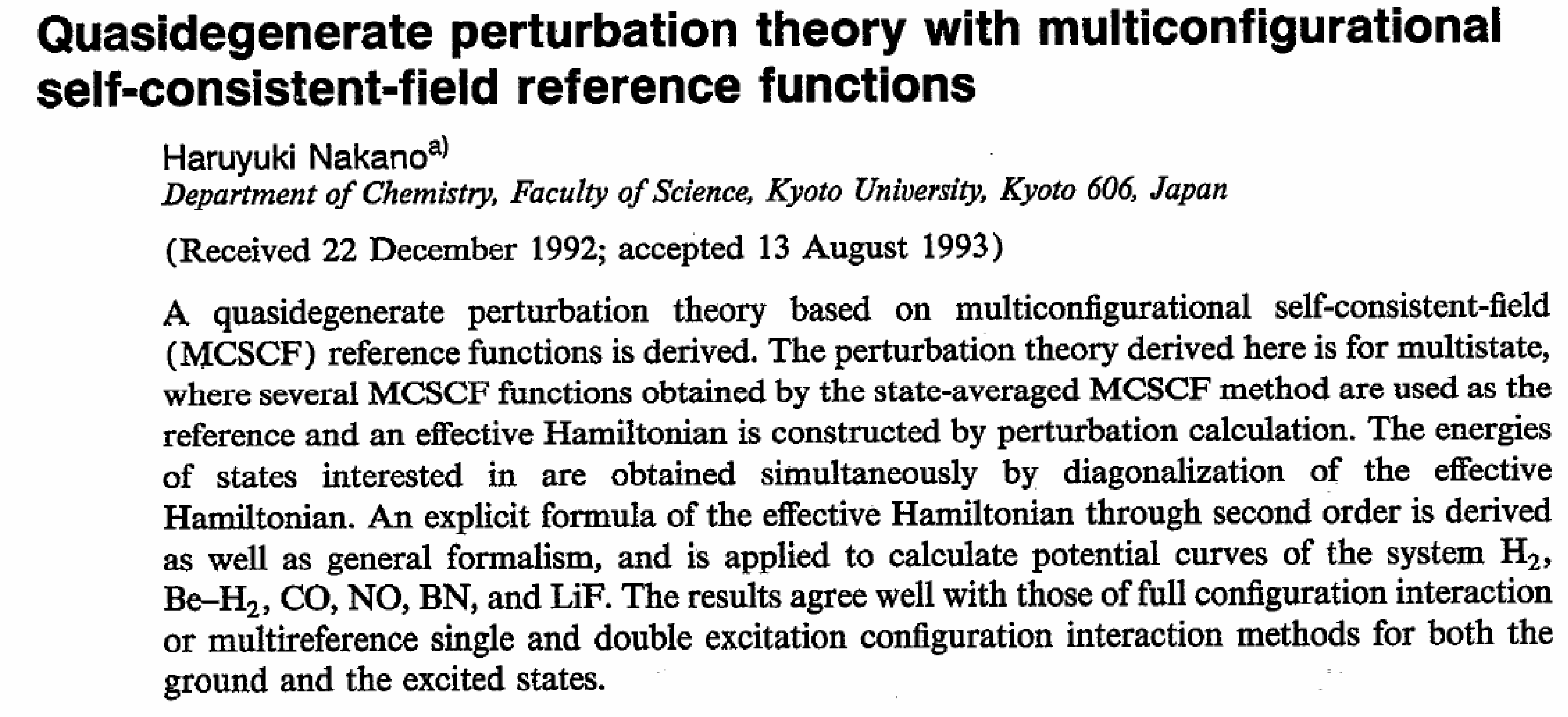
- ***There are some internal flaws in the formulation of this theory!***

MCQDPT: analysis

MCQDPT: primary paper



J. Chem. Phys., Vol. 99, No. 10, 15 November 1993



Quasidegenerate perturbation theory with multiconfigurational self-consistent-field reference functions

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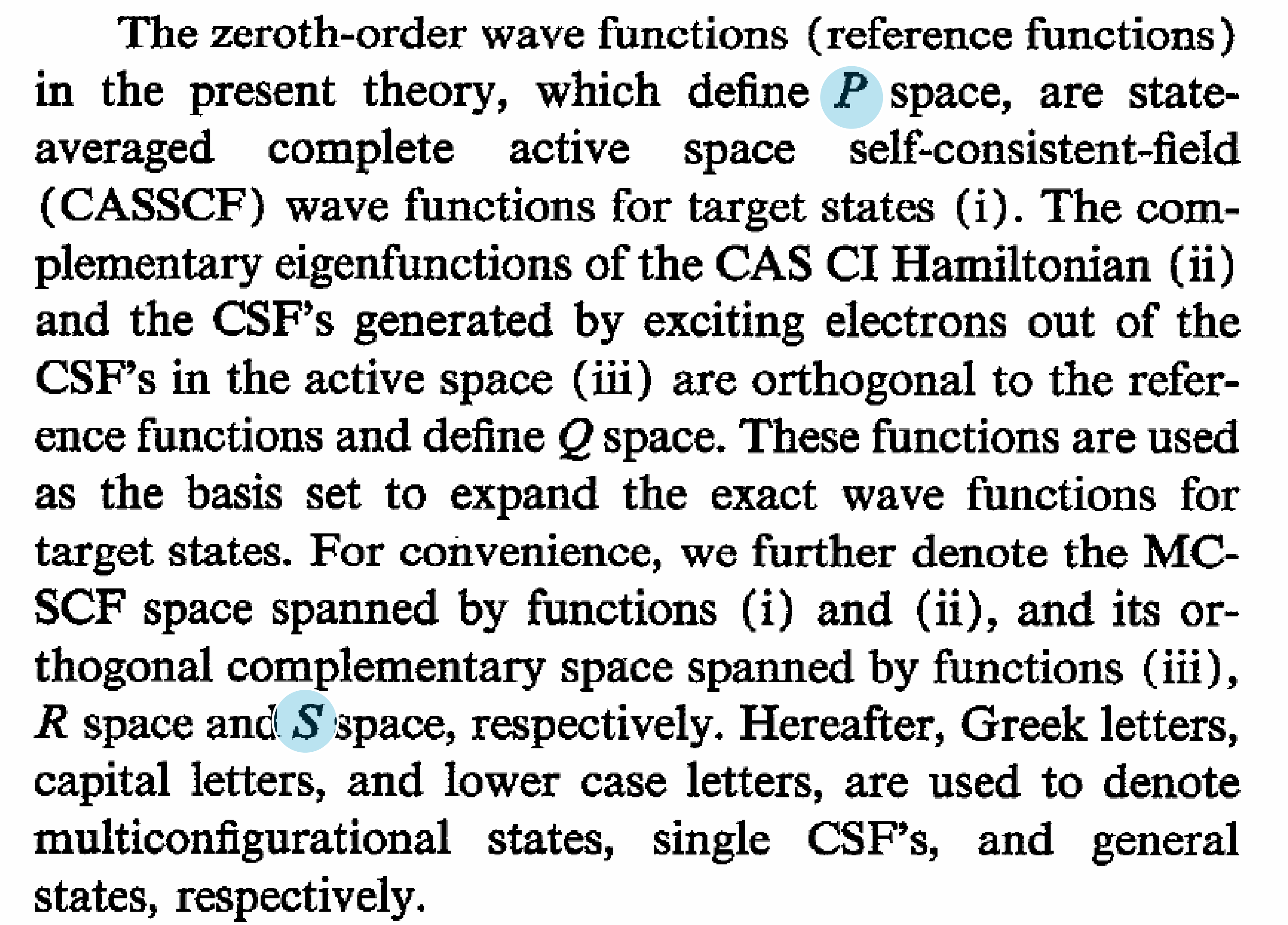
(Received 22 December 1992; accepted 13 August 1993)

A quasidegenerate perturbation theory based on multiconfigurational self-consistent-field (MCSCF) reference functions is derived. The perturbation theory derived here is for multistate, where several MCSCF functions obtained by the state-averaged MCSCF method are used as the reference and an effective Hamiltonian is constructed by perturbation calculation. The energies of states interested in are obtained simultaneously by diagonalization of the effective Hamiltonian. An explicit formula of the effective Hamiltonian through second order is derived as well as general formalism, and is applied to calculate potential curves of the system H_2, Be–H_2, CO, NO, BN, and LiF. The results agree well with those of full configuration interaction or multireference single and double excitation configuration interaction methods for both the ground and the excited states.

MCQDPT: basics

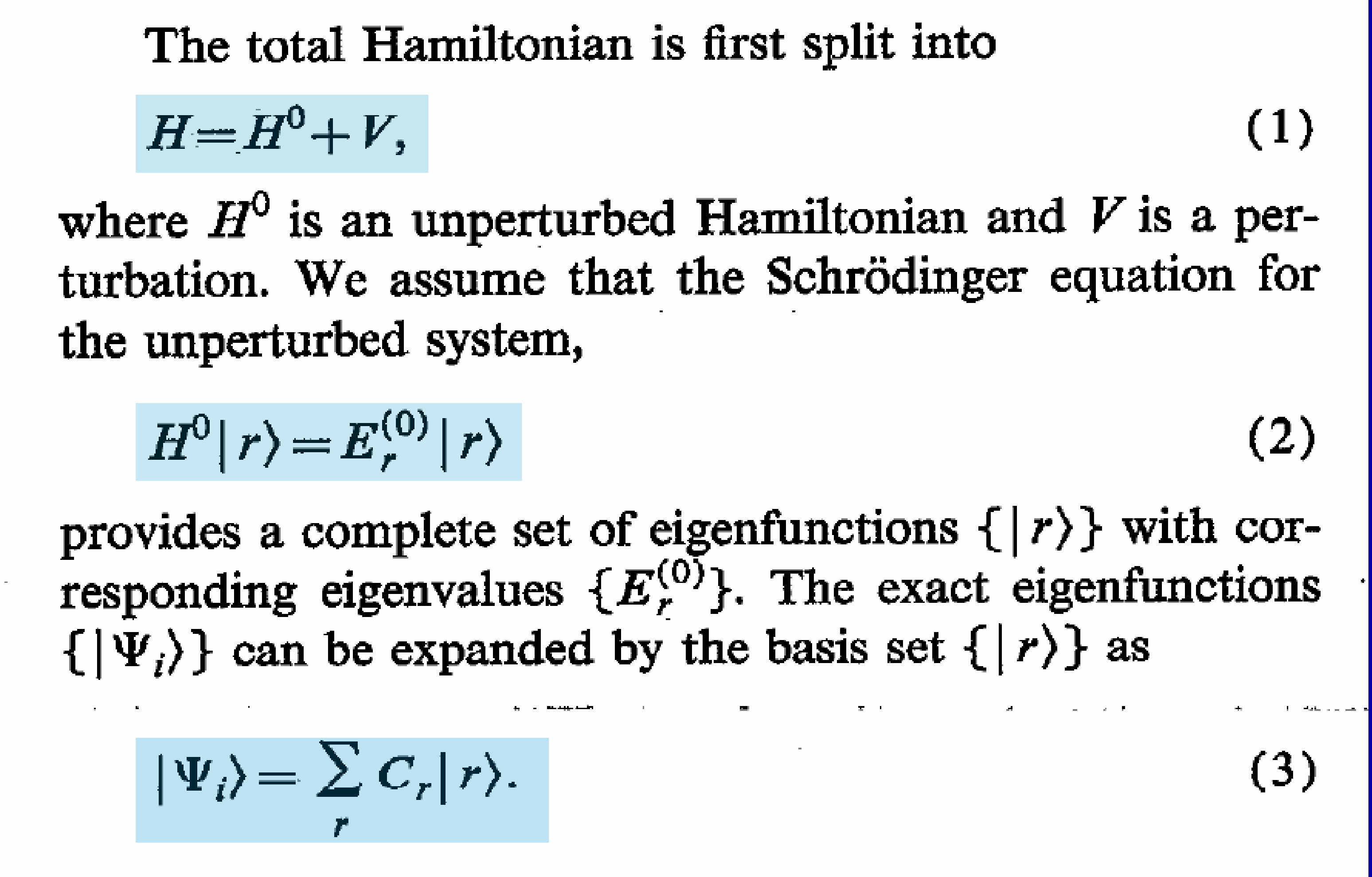
- PT of partially contracted type
- Theory with Unitary normalization
  - Van Vleck type PT
- Note that the derivation of PT equations in the primary paper is not quite correct
  - The correct one will be reported elsewhere
- Some of the basic equations are nevertheless correct in the primary paper
  - *But not all of them as will be shown below!*

MCQDPT: basic subspaces



The zeroth-order wave functions (reference functions) in the present theory, which define P space, are state-averaged complete active space self-consistent-field (CASSCF) wave functions for target states (i). The complementary eigenfunctions of the CAS CI Hamiltonian (ii) and the CSF's generated by exciting electrons out of the CSF's in the active space (iii) are orthogonal to the reference functions and define Q space. These functions are used as the basis set to expand the exact wave functions for target states. For convenience, we further denote the MC-SCF space spanned by functions (i) and (ii), and its orthogonal complementary space spanned by functions (iii), R space and S space, respectively. Hereafter, Greek letters, capital letters, and lower case letters, are used to denote multiconfigurational states, single CSF's, and general states, respectively.

MCQDPT: some trivial stuff



The total Hamiltonian is first split into

$$H = H^0 + V, \tag{1}$$

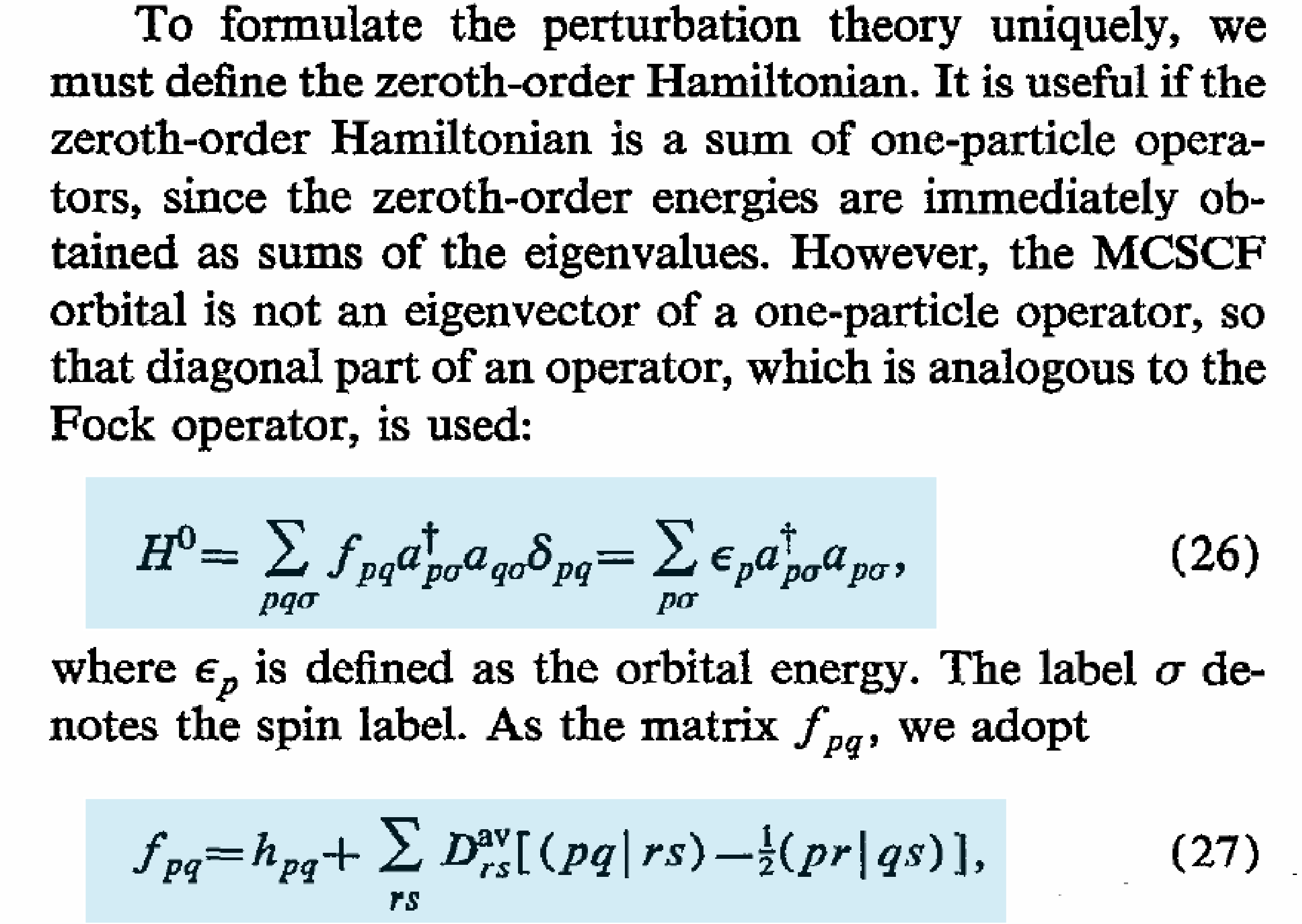
where H^0 is an unperturbed Hamiltonian and V is a perturbation. We assume that the Schrödinger equation for the unperturbed system,

$$H^0|r\rangle = E_r^{(0)}|r\rangle \tag{2}$$

provides a complete set of eigenfunctions $\{|r\rangle\}$ with corresponding eigenvalues $\{E_r^{(0)}\}$. The exact eigenfunctions $\{|\Psi_i\rangle\}$ can be expanded by the basis set $\{|r\rangle\}$ as

$$|\Psi_i\rangle = \sum_r C_r|r\rangle. \tag{3}$$

MCQDPT: choice of H^0



To formulate the perturbation theory uniquely, we must define the zeroth-order Hamiltonian. It is useful if the zeroth-order Hamiltonian is a sum of one-particle operators, since the zeroth-order energies are immediately obtained as sums of the eigenvalues. However, the MCSCF orbital is not an eigenvector of a one-particle operator, so that diagonal part of an operator, which is analogous to the Fock operator, is used:

$$H^0 = \sum_{pq\sigma} f_{pq} a^\dagger_{p\sigma} a_{q\sigma} \delta_{pq} = \sum_{p\sigma} \epsilon_p a^\dagger_{p\sigma} a_{p\sigma}, \qquad (26)$$

where ϵ_p is defined as the orbital energy. The label σ denotes the spin label. As the matrix f_{pq}, we adopt

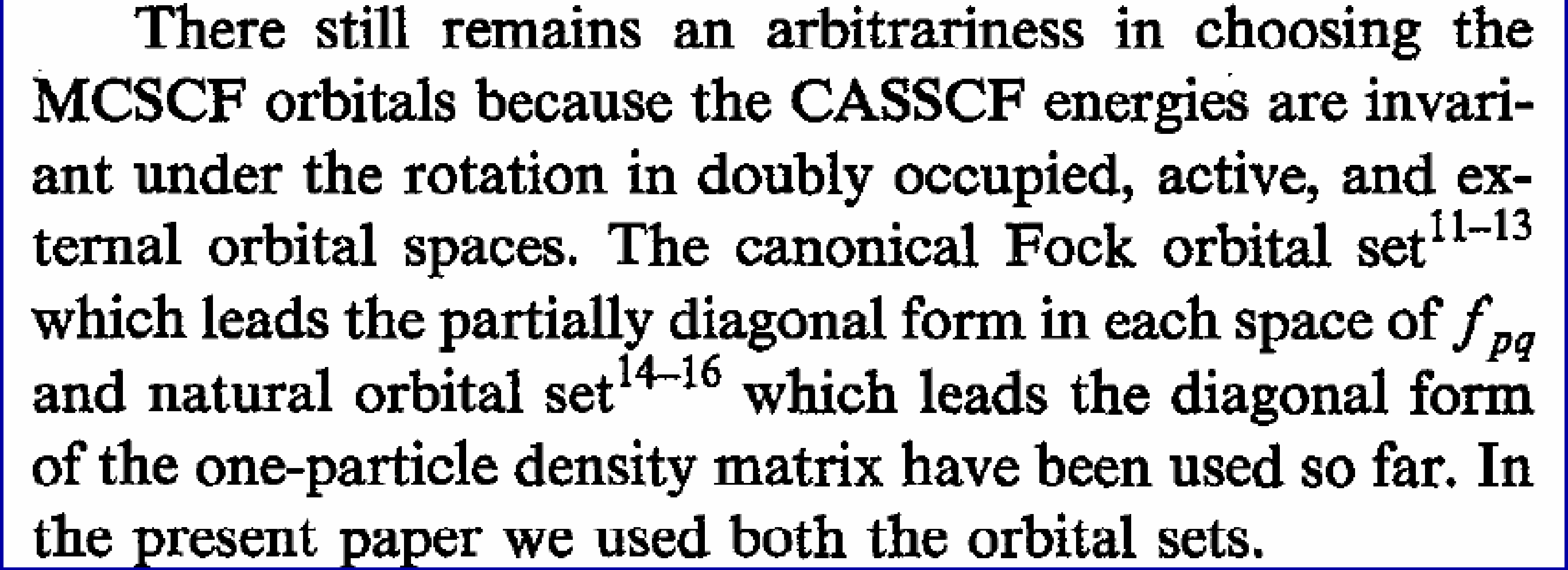
$$f_{pq} = h_{pq} + \sum_{rs} D^{\mathrm{av}}_{rs}[(pq|rs) - \tfrac{1}{2}(pr|qs)], \qquad (27)$$

where D^{av}_{rs} denotes state-averaged one-particle density matrix.

Note made in pass: important drawback of all MCQDPT-like approaches

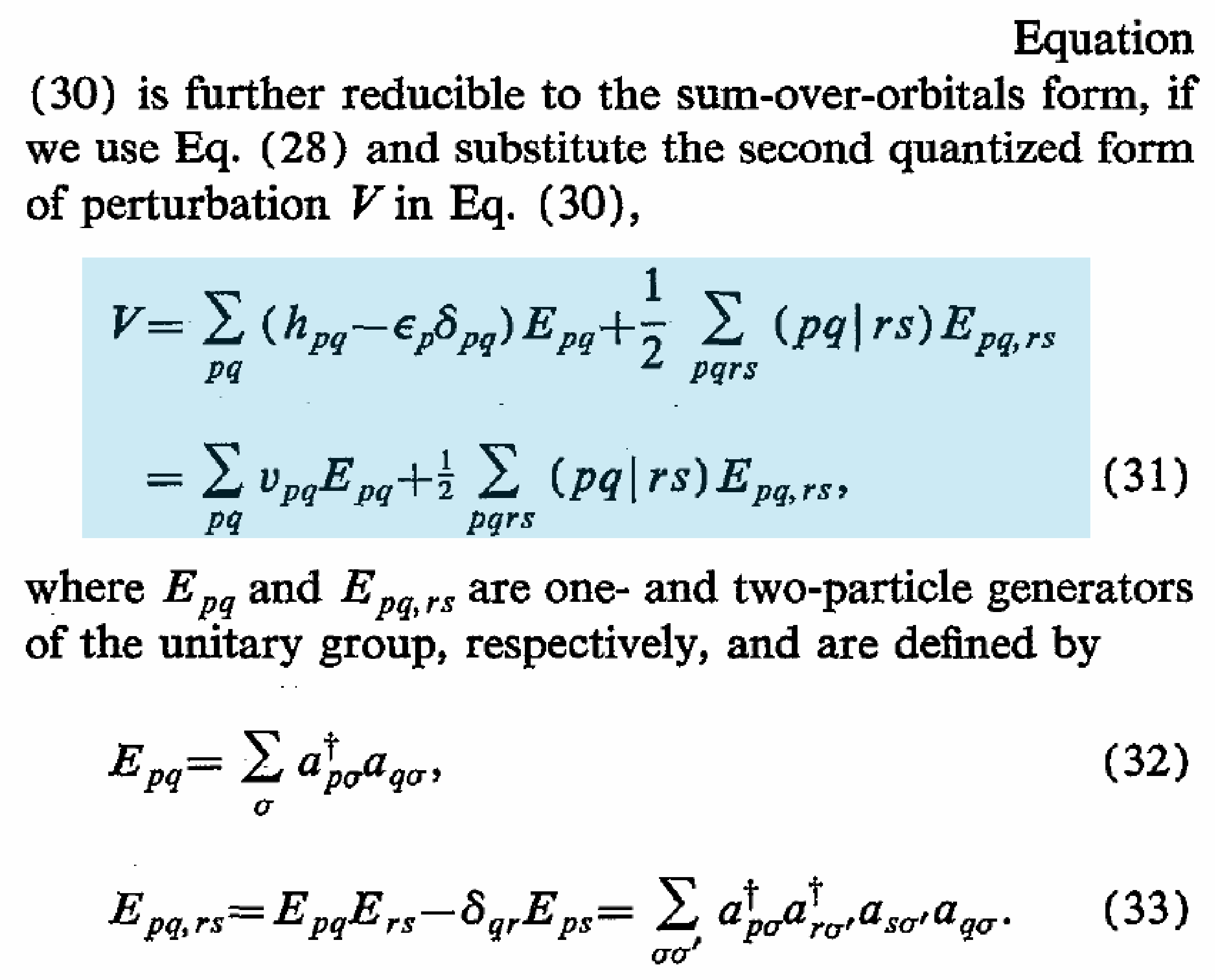
- ***The oversimplified choice of H^0 makes theory absolutely non-invariant***
  - ***This causes lots of problems actually…***

MCQDPT: choice of orbitals



There still remains an arbitrariness in choosing the MCSCF orbitals because the CASSCF energies are invariant under the rotation in doubly occupied, active, and external orbital spaces. The canonical Fock orbital set[11–13] which leads the partially diagonal form in each space of f_{pq} and natural orbital set[14–16] which leads the diagonal form of the one-particle density matrix have been used so far. In the present paper we used both the orbital sets.

MCQDPT: perturbation



Equation (30) is further reducible to the sum-over-orbitals form, if we use Eq. (28) and substitute the second quantized form of perturbation V in Eq. (30),

$$V=\sum_{pq}(h_{pq}-\epsilon_p\delta_{pq})E_{pq}+\frac{1}{2}\sum_{pqrs}(pq|rs)E_{pq,rs}$$

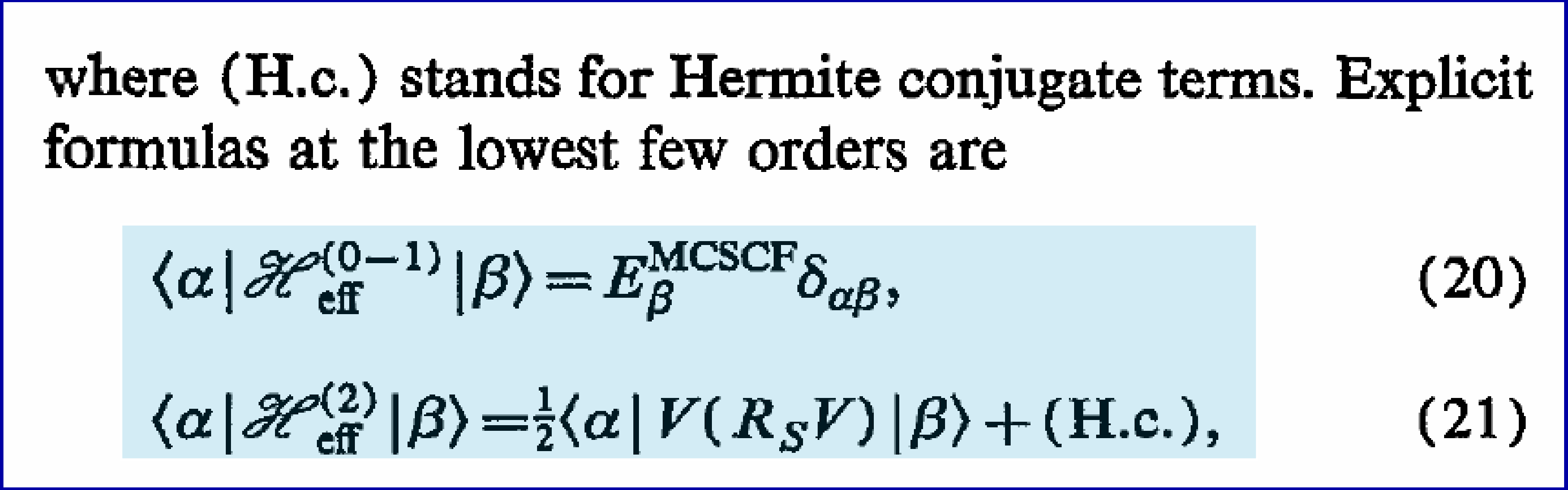
$$=\sum_{pq}v_{pq}E_{pq}+\tfrac{1}{2}\sum_{pqrs}(pq|rs)E_{pq,rs}, \qquad (31)$$

where E_{pq} and $E_{pq,rs}$ are one- and two-particle generators of the unitary group, respectively, and are defined by

$$E_{pq}=\sum_{\sigma}a^{\dagger}_{p\sigma}a_{q\sigma}, \qquad (32)$$

$$E_{pq,rs}=E_{pq}E_{rs}-\delta_{qr}E_{ps}=\sum_{\sigma\sigma'}a^{\dagger}_{p\sigma}a^{\dagger}_{r\sigma'}a_{s\sigma'}a_{q\sigma}. \qquad (33)$$

MCQDPT2: more trivial stuff

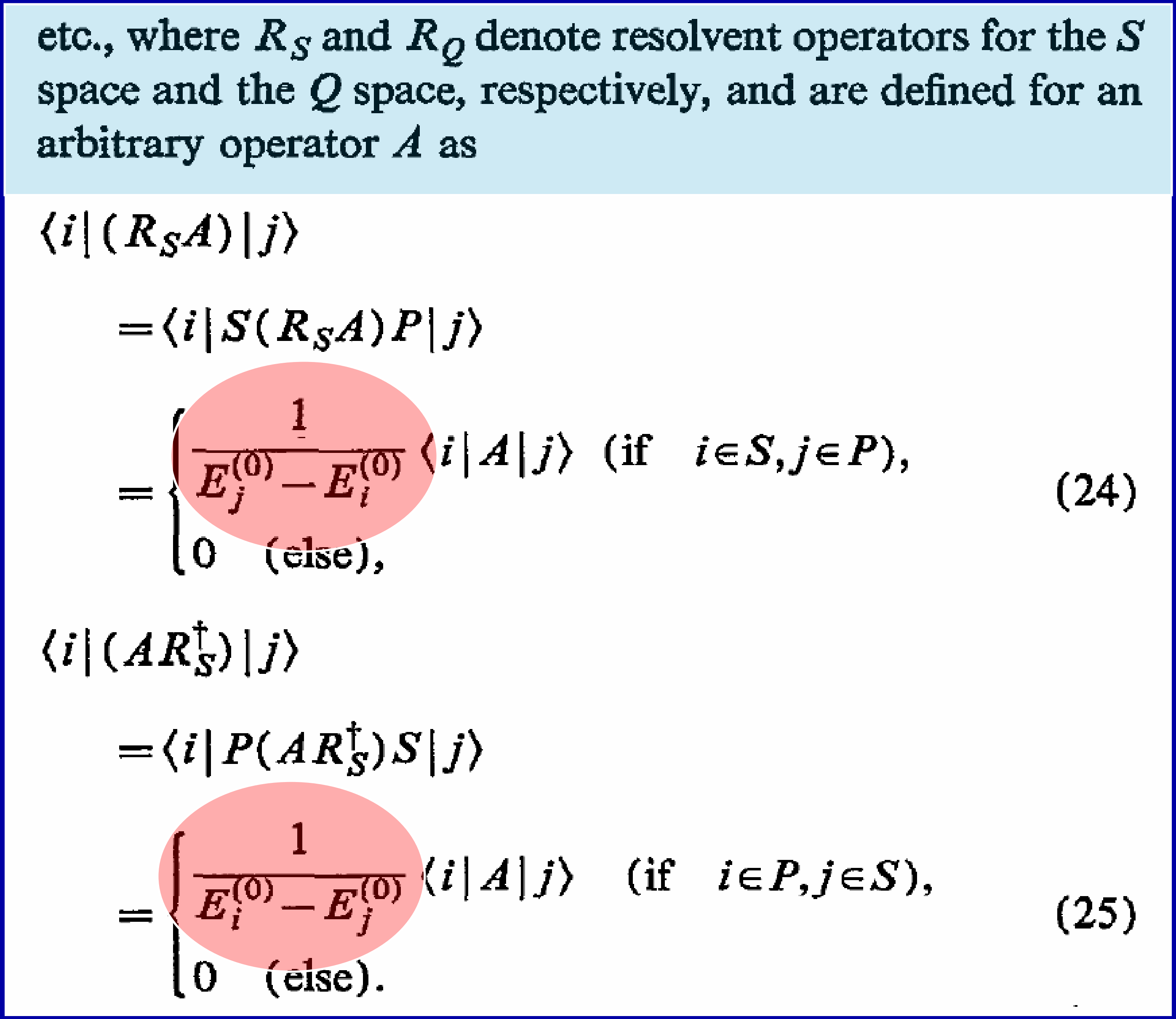


where (H.c.) stands for Hermite conjugate terms. Explicit formulas at the lowest few orders are

$$\langle\alpha|\mathscr{H}_{\text{eff}}^{(0-1)}|\beta\rangle = E_{\beta}^{\text{MCSCF}}\delta_{\alpha\beta}, \tag{20}$$

$$\langle\alpha|\mathscr{H}_{\text{eff}}^{(2)}|\beta\rangle = \tfrac{1}{2}\langle\alpha|V(R_S V)|\beta\rangle + (\text{H.c.}), \tag{21}$$

MCQDPT: trivial mistake!

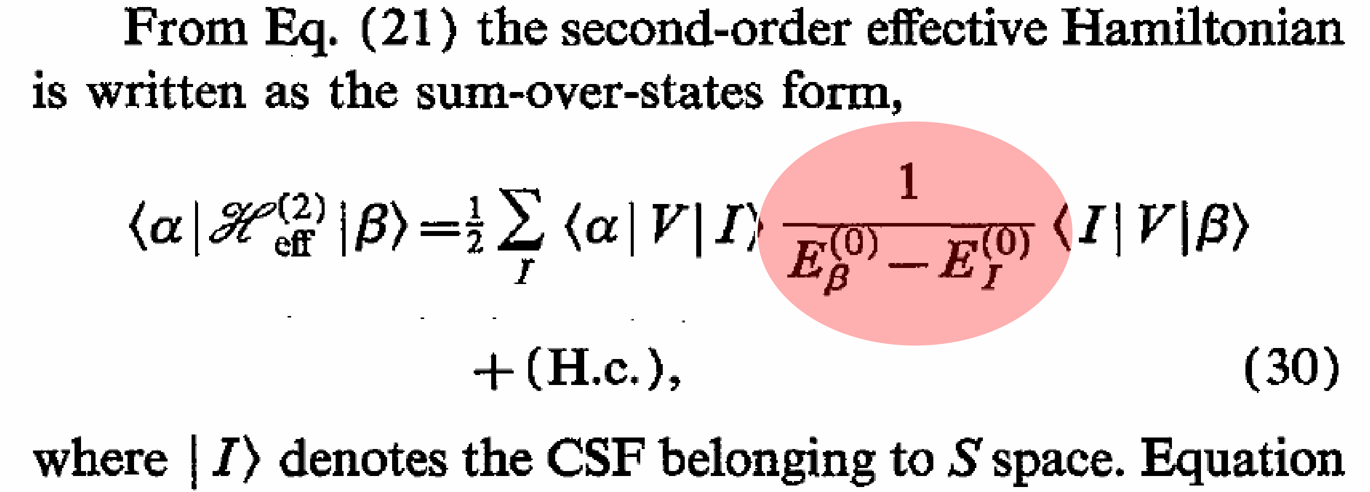


etc., where R_S and R_Q denote resolvent operators for the S space and the Q space, respectively, and are defined for an arbitrary operator A as

$$\begin{aligned}\langle i|(R_S A)|j\rangle &= \langle i|S(R_S A)P|j\rangle \\ &= \begin{cases} \dfrac{1}{E_j^{(0)} - E_i^{(0)}} \langle i|A|j\rangle & (\text{if} \quad i\in S, j\in P), \\ 0 & (\text{else}), \end{cases}\end{aligned} \tag{24}$$

$$\begin{aligned}\langle i|(A R_S^\dagger)|j\rangle &= \langle i|P(A R_S^\dagger)S|j\rangle \\ &= \begin{cases} \dfrac{1}{E_i^{(0)} - E_j^{(0)}} \langle i|A|j\rangle & (\text{if} \quad i\in P, j\in S), \\ 0 & (\text{else}). \end{cases}\end{aligned} \tag{25}$$

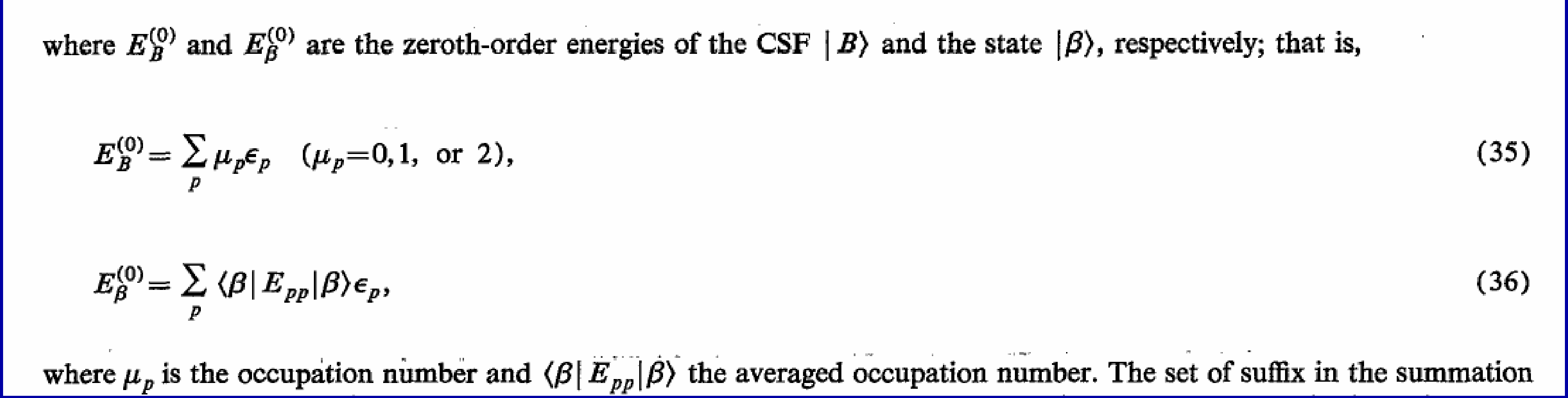
MCQDPT2: where the error is



From Eq. (21) the second-order effective Hamiltonian is written as the sum-over-states form,

$$\langle\alpha|\mathscr{H}^{(2)}_{\text{eff}}|\beta\rangle=\tfrac{1}{2}\sum_{I}\langle\alpha|V|I\rangle\frac{1}{E_{\beta}^{(0)}-E_{I}^{(0)}}\langle I|V|\beta\rangle+(\text{H.c.}), \qquad (30)$$

where $|I\rangle$ denotes the CSF belonging to S space. Equation



where $E_B^{(0)}$ and $E_\beta^{(0)}$ are the zeroth-order energies of the CSF $|B\rangle$ and the state $|\beta\rangle$, respectively; that is,

$$E_B^{(0)}=\sum_p \mu_p\epsilon_p \quad (\mu_p=0,1,\ \text{or}\ 2), \qquad (35)$$

$$E_\beta^{(0)}=\sum_p \langle\beta|E_{pp}|\beta\rangle\epsilon_p, \qquad (36)$$

where μ_p is the occupation number and $\langle\beta|E_{pp}|\beta\rangle$ the averaged occupation number. The set of suffix in the summation

Why (and where) the error is?

- **Expression for resolvent is wrong!**
- **The expressions above (as well as all other equations in primary MCQDPT paper) assumes fully diagonal (and fully one-body) H^0, both in P and S spaces**
  - ***This is NOT TRUE in the case of MCQDPT theory!***

MCQDPT: examining H^0

$$H^0 = \sum_{pq\sigma} f_{pq} a^\dagger_{p\sigma} a_{q\sigma} \delta_{pq} = \sum_{p\sigma} \epsilon_p a^\dagger_{p\sigma} a_{p\sigma}$$

- ***H^0 is indeed diagonal in the basis of determinants or CSFs!***
  - ***In particular, it is diagonal in S space***
  - ***The SP and PS blocks are indeed zero***
- ***However, it is not diagonal in P space!***
  - ***Proof (trivial):***

$$E_B^0 = E_{core} + \sum_{\substack{active\\orbitals}} n_i(B)\varepsilon_i \qquad E_\beta^0 = H^0_{\beta\beta} = \sum_B \left|C_B^\beta\right|^2 E_B^0$$

$$H^0_{\alpha\beta} = \sum_B C_B^{\alpha+} C_B^{\beta} E_B^0 \neq 0, \text{ and thus } H^0_{PP} \text{ is not diagonal!}$$

MCQDPT: the Farewell

- *H^0 is “slightly” non-diagonal*
  - *Expression for resolvent is not correct*
- *From this point now on the rest of all MCQDPT working equations is absolutely senseless*
- *Hence, any essentially MCQDPT2 type (not just MR-MP2-like) results obtained so far are in turn just more or less erroneous*
- *Finally, this makes MCQDPT as well as DETPT and their generalization for non-CAS type MCSCF simply the completely senseless and useless “theories” that should not be used anymore*
  - *However, see Appendix I if you still like MCQDPT*

MCQDPT mortuus est, vivat XMCQDPT!

- ***XMCQDPT***
  - – ***Just the correctly formulated MCQDPT that explicitly takes into account the non-diagonality of H^0_{pp}***
  - – ***H^0 is exactly as given by Eqs. 26-27***
    - ***Strictly one-particle operator***
  - – ***V is exactly as given by Eq. 31***
- ***XMCQDPT2***
  - – ***Only P-S energy contributions are nonzero at second order***
    - ***See Appendix II for the rigorous proof of vanishing all pure intra-CAS contributions at second (and higher) orders***
  - – ***Unlike MCQDPT2, straightforward implementation requires solution of huge number of small (with N_{eff} by N_{eff} matrix) systems of linear equations instead of direct summation over states***
    - ***Straightforward approach would then mean the death of Firefly's ultra-fast direct summation code***
    - ***XMCQDPT2 in Firefly uses more clever approach!***

XMCQDPT2 in Firefly – the clever approach

- **If**

$$H = \begin{bmatrix} H_{pp}^0 + V_{pp} & H_{ps} \\ H_{sp} & H_{ss}^0 + V_{ss} \end{bmatrix}$$

- **Then, using Van Vleck-type PT expansion one gets (see Appendix II for methodology) :**

$$h_0 = H_{pp}^0, \qquad h_1 = V_{pp},$$

$$h_2 = \frac{1}{2}[H_{ps} v_1 + v_1^+ H_{sp}], \text{ where } v_1 \text{ is defined}$$

$$\text{by the following linear equation :}$$

$$H_{sp} + H_{ss}^0 v_1 = v_1 H_{pp}^0$$

After some simple math

If $H_{sp} + H_{ss}^{0} v_1 = v_1 H_{pp}^{0}$ is held, then:

$$H_{sp} O + H_{ss}^{0} (v_1 O) = (v_1 O)(O^{+} H_{pp}^{0} O)$$

Using $h_2 = \frac{1}{2}[H_{ps} v_1 + v_1^{+} H_{sp}]$, one gets:

$$O^{+} h_2 O = \frac{1}{2}[(O^{+} H_{ps})(v_1 O) + (O^{+} v_1^{+})(H_{sp} O)]$$

What this mean is:

- *h_2 has trivial (and very nice) transformation properties with respect to rotations of basis in model space!*
- *We just need to diagonalize H^0_{pp} and transform reference CI vectors accordingly:*
  - *H^0 is now fully diagonal in S+P!*
  - *The working equations of MCQDPT2 do not assume the reference vectors are CI eigenvectors!*
- *Thus, we can easily apply the existing state-of-the-art Firefly's MCQDPT2 code to perform XMCQDPT2 calculations by using rotated CI vectors (intermediate basis)!*

Some nice XMCQDPT2 properties

- *True 1-particle MP2-like H^0*
- *Nice invariance properties*
- *Completely equivalent to MR-MP2 for single-reference case*
- *Unlike MCQDPT2 it is stable with respect to model space extension*
  - *The limit is just the fully uncontracted theory*
- *Does not result in artificially large off-diagonal elements*
  - *Note – large off-diagonal element of H^0_{pp} typically corresponds to large off-diagonal in MCQDPT2 calculations*
    - *We can predict MCQDPT2 failures by just examining H^0_{pp}!*
- *Gives very good results typically*
  - *We already have statistics over hundreds of tests*

XMCQDPT2: Retinal sample

```
*** MATRIX H(0)pp ***

              1           2

   1 -681.5735897
   2    -0.0654530-681.3809372

*** CI TO INTERMEDIATE BASIS TRANSFORMATION MATRIX ***

              1           2

   1     0.9558037  -0.2940056
   2     0.2940056   0.9558037
```

XMCQDPT2: Retinal sample

```
############################
###   MC-XQDPT2 RESULTS  ###
############################
*** EFFECTIVE HAMILTONIAN (0-2) ***
-----------------------------------
                  1            2
    1 -9.897413D+02
    2 -6.406494D-03-9.896682D+02
```

S0-S1 transition energy: 614 nm!

XMCQDPT: how to do?

- It’s simply with Firefly:
  - Just use $XMCQDPT instead of $MCQDPT
    - All keywords are the same as in $MCQDPT group
    - And sure it works with $mcqfit as well

Credits

- ***Dr. Vladimir I. Pupyshev***

Thank you for your attention!

Appendix I
The true H^0 used in derivation of MCQDPT2 theory

MCQDPT2: is not quite dead yet

- For the very specific choice of H^0, as well as the specific basis in P space, the MCQDPT2 equations are still valid!
- Let:
  - P denotes the model space spanned by reference CI vectors,
    - ***Important: basis in P is formed by the reference CI vectors themselves***
  - Q denotes the complement of P inside CAS
  - S denotes the set of singly and doubly excited CSFs or determinants taking all CSFs from CAS space as references

MCQDPT2: true *H^0*

- Let's denote true ***H^0*** of MCQDPT2 as ***H^0_{true}***, as opposed to ***H^0*** given by Eq. 26
- P-P block: ***H^0_{true}*** is diagonal and is:

$$H^{0}{}_{pp}^{true} = \sum_{\alpha} |\alpha\rangle\langle\alpha| H^0 |\alpha\rangle\langle\alpha|$$

  - where summation runs over CI vectors in model space

MCQDPT2: true H^0

- P-Q (Q-P) and Q-Q blocks are arbitrary (see Appendix II)
- S-S block:

$$H^0_{ss}{}^{true} = H^0_{ss}$$

- All other blocks are zero

MCQDPT2: true H^0 drawbacks

- H^0_{true} is absolutely non-invariant
- It is evident that by this definition H^0_{true} is many-particle operator for any non-trivial model space
  - Hence, the perturbation is many-particle operator as well
- Seems to be the main sources of problems

Appendix II
Rigorous proof of the absence of intra-CAS interaction at second order of XMCQDPT (very trivial fact actually)

Notations

- ***P*** is the model subspace, spanned by reference CAS vectors
- ***Q*** is the ***I*–*P*** subspace, where ***I*** is the identity inside of the CAS Hamiltonian
- The particular choice of basis set inside P or Q is arbitrary

Proof: Hamiltonian

$$H = \begin{bmatrix} H_{pp}^{0} + V_{pp} & H_{pq}^{0} + V_{pq} \\ H_{qp}^{0} + V_{qp} & H_{qq}^{0} + V_{qq} \end{bmatrix}$$

$V_{qp} = -H_{qp}^{0}$ as offdiagonal

blocks of H are zero

Proof: what we are searching for

$$U^{+}HU = H_{eff}$$

$$\text{where}: \quad U^{+}U = 1$$

For known U, UU$_0$ is also solution for some unitary U$_0$
Hence, there is some freedom in choice of U

Proof: expansion for U

$$U = \begin{bmatrix} u \\ v \end{bmatrix} = \begin{bmatrix} 1 + u_1 + u_2 + \ldots \\ v_1 + v_2 + \ldots \end{bmatrix}$$

Proof: U^+U condition

$$\begin{bmatrix} 1+u_1+u_2+\ldots \\ v_1+v_2+\ldots \end{bmatrix}^+ \begin{bmatrix} 1+u_1+u_2+\ldots \\ v_1+v_2+\ldots \end{bmatrix} = \begin{bmatrix} 1+u_1^{\,+}+u_2^{\,+}+\ldots, & v_1^{\,+}+v_2^{\,+}+\ldots \end{bmatrix} \begin{bmatrix} 1+u_1+u_2+\ldots \\ v_1+v_2+\ldots \end{bmatrix} = 1$$

This means that:

$$(1+u_1^{\,+}+u_2^{\,+}+\ldots)(1+u_1+u_2+\ldots)+(v_1^{\,+}+v_2^{\,+}+\ldots)(v_1+v_2+\ldots)=1$$

$$1+u_1^{\,+}+u_1+u_2^{\,+}+u_2+v_1^{\,+}v_1+u_1^{\,+}u_1+\ldots=1$$

And hence:

$$u_1^{\,+}+u_1=0, \qquad u_2^{\,+}+u_2+v_1^{\,+}v_1+u_1^{\,+}u_1\ldots=0 \qquad (\text{Eq.}1)$$

Proof: choice of u_1 and u_2

- u_1 is square anti-Hermitian
- ***U_0*** above is arbitrary and thus we can define u_1 as needed for simpler expressions
- Let's choose $u_1 = 0$
- Eq. 1 does not impose any restrictions on anti-Hermitian part of u_2
  - Let's choose u_2 to be symmetric
    - Simply corresponds taking ***$U_0 = I$*** up to second order:

$$u_2^{+} = u_2, \qquad u_2 = -\frac{1}{2} v_1^{+} v_1 \quad (\text{Eq. } 2)$$

Proof: equation for *H*_{eff}

$$H_{eff} = U^{+}HU = \begin{bmatrix} 1+u_2^{+}+\ldots, & v_1^{+}+v_2^{+}+\ldots \end{bmatrix} \begin{bmatrix} H_{pp}^{0}+V_{pp} & H_{pq}^{0}+V_{pq} \\ H_{qp}^{0}+V_{qq} & H_{qq}^{0}+V_{qq} \end{bmatrix} \begin{bmatrix} 1+u_2+\ldots \\ v_1+v_2+\ldots \end{bmatrix} =$$

$$= \begin{bmatrix} 1+u_2^{+}+\ldots, & v_1^{+}+v_2^{+}+\ldots \end{bmatrix} \begin{bmatrix} H_{pp}^{0}+V_{pp}+H_{pp}^{0}u_2+(H_{pq}^{0}+V_{pq})v_1+H_{pq}^{0}v_2+\ldots \\ H_{qp}^{0}+V_{qp}+H_{qp}^{0}u_2+H_{qq}^{0}v_1+V_{qq}v_1+H_{qq}^{0}v_2+\ldots \end{bmatrix} =$$

$$= (1+u_2^{+}+\ldots)(H_{pp}^{0}+V_{pp}+H_{pp}^{0}u_2+(H_{pq}^{0}+V_{pq})v_1+H_{pq}^{0}v_2+\ldots)$$

$$+(v_1^{+}+v_2^{+}+\ldots)(H_{qp}^{0}+V_{qp}+H_{qp}^{0}u_2+H_{qq}^{0}v_1+V_{qq}v_1+H_{qq}^{0}v_2+\ldots) =$$

$$= H_{pp}^{0}+V_{pp}+H_{pp}^{0}u_2+H_{pq}^{0}v_1+V_{pq}v_1+H_{pq}^{0}v_2+u_2^{+}H_{00}^{0}$$

$$+v_1^{+}H_{qp}^{0}+v_1^{+}V_{pq}+v_1^{+}H_{qq}^{0}v_1+v_2^{+}H_{qp}^{0}+\ldots \quad \text{(Eq. 3)}$$

Proof: H_{eff} expansion

$$H_{eff} = H_{eff}{}^{0} + H_{eff}{}^{1} + H_{eff}{}^{2} + \ldots \text{(Eq. 4)}$$

From Eq. 3:

$$H_{eff}{}^{0} = H^{0}_{pp} \quad \text{(Eq. 5)}$$

$$H_{eff}{}^{1} = V_{pp} + H^{0}_{pq} v_1 + v_1{}^{+} H^{0}_{qp} \quad \text{(Eq. 6)}$$

$$H_{eff}{}^{2} = H^{0}_{pp} u_2 + u_2{}^{+} H^{0}_{pp} + v_1{}^{+} H^{0}_{qq} v_1 +$$

$$+ H^{0}_{pq} v_2 + V_{pq} v_1 + v_1{}^{+} V_{qp} + v_2{}^{+} H^{0}_{qp} \text{ (Eq. 7)}$$

Proof: using $HU=UH_{eff}$ identity

$$\begin{bmatrix} H^{0}_{pp}+V_{pp} & H^{0}_{pq}+V_{pq} \\ H^{0}_{qp}+V_{qp} & H^{0}_{qq}+V_{qq} \end{bmatrix} \begin{bmatrix} 1+u_2+\dots \\ v_1+v_2+\dots \end{bmatrix} =$$

$$\begin{bmatrix} 1+u_2+\dots \\ v_1+v_2+\dots \end{bmatrix} [H_{eff}{}^{0}+H_{eff}{}^{1}+H_{eff}{}^{2}+\dots]$$

or

$$\begin{bmatrix} H^{0}_{pp}+V_{pp}+H^{0}_{pq}v_1+V_{pq}v_1+H^{0}_{pp}u_2+H^{0}_{pq}v_2+\dots \\ H^{0}_{qp}+V_{qp}+H^{0}_{qq}v_1+H^{0}_{qp}u_2+V_{qq}v_1+H^{0}_{qq}v_2+\dots \end{bmatrix} =$$

$$\begin{bmatrix} H_{eff}{}^{0}+H_{eff}{}^{1}+H_{eff}{}^{2}+u_2H_{eff}{}^{0}+\dots \\ v_1H_{eff}{}^{0}+v_1H_{eff}{}^{1}+v_2H_{eff}{}^{0}+\dots \end{bmatrix}$$

Proof: using $HU=UH_{eff}$ identity

$$\begin{bmatrix} H^0_{pp}+V_{pp}+H^0_{pq}v_1+V_{pq}v_1+H^0_{pp}u_2+H^0_{pq}v_2+\ldots \\ H^0_{qp}+V_{qp}+H^0_{qq}v_1+H^0_{qp}u_2+V_{qq}v_1+H^0_{qq}v_2+\ldots \end{bmatrix} =$$

$$\begin{bmatrix} H_{eff}{}^0+H_{eff}{}^1+H_{eff}{}^2+u_2H_{eff}{}^0+\ldots \\ v_1H_{eff}{}^0+v_1H_{eff}{}^1+v_2H_{eff}{}^0+\ldots \end{bmatrix}$$

means

$$H^0_{pp}+V_{pp}+H^0_{pq}v_1+V_{pq}v_1+H^0_{pp}u_2+H^0_{pq}v_2+\ldots=H_{eff}{}^0+H_{eff}{}^1+H_{eff}{}^2+u_2H_{eff}{}^0+\ldots$$

and

$$H^0_{qp}+V_{qp}+H^0_{qq}v_1+H^0_{qp}u_2+V_{qq}v_1+H^0_{qq}v_2+\ldots=v_1H_{eff}{}^0+v_1H_{eff}{}^1+v_2H_{eff}{}^0+\ldots$$

(Eqs. 8)

Proof: Eqs 6 and 8

$$H_{eff}{}^{1} = V_{pp} + H^{0}_{pq} v_1 + v_1{}^{+} H^{0}_{qp}$$

and

$$H_{eff}{}^{1} = V_{pp} + H^{0}_{pq} v_1$$

and

$$H^{0}_{qp} = v_1 H_{eff}{}^{0} - H^{0}_{qq} v_1 - V_{qp} = v_1 H^{0}_{pp} - H^{0}_{qq} v_1 - V_{qp}$$

and hence:

$$H_{eff}{}^{1} = V_{pp},$$

$$v_1 \equiv 0,\ \ u_2 \equiv 0, \quad (\mathrm{Eqs.\,9})$$

Proof: Eqs 7, 8, and 9

$H_{eff}{}^{2} = H_{pq}^{0} v_2 + v_2{}^{+} H_{qp}^{0}$ **and** $H_{eff}{}^{2} = H_{pq}^{0} v_2$

$$\Rightarrow \; H_{pq}^{0} v_2 = v_2{}^{+} H_{qp}^{0} = 0$$

$$\Rightarrow H_{eff}{}^{2} = 0$$