# Relativistic GVVPT2 via MOLCAS-UNDMOL Tandem

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We have implemented relativisitic GVVPT2 using DKH integrals and ANO-RCC basis sets from Molcas package. It is done by developing an interface code accessing, re-ordering and transforming one- and two-electron integral array, making it available for any method implemented within the UNDMol package. The relativistic GVVPT2 is applied to calculations of ground and excited states potential energy curves of TiC and CrH.

# ACCESSING MOLCAS INTEGRALS

- Fortran 77
- Module Seward generates One and Two electron integrals in SAO (symmetrized atomic orbitals) basis, symmetry blocked.
- Provides Fortran 77 API to access integrals
  - `call iRdOne(iretcode,iopt,label,icomp,len,isym`
  - `iopt:getsize/read array,len:  size of the array,components of integrals (X,Y..)`
  - `call OpnOrd(iretc,iopt,'ORDINT',lunit)`
  - `call RdOrd(iretc,iopt,isym,jsym,ksym,lsym,buffer,klbl,nmat)`
- Relativistic Integrals, ANO-RCC basis is available.

# UNDMOL PACKAGE

- Written in C
- Module AOINTS generate one- and two-electron integrals in AO basis; AO symmetry is not taken into account.
- Simple and straight forward integral file format:

```
 struct twoel_integral
{
  int iao,jao,kao,lab;
  double val;
};
struct twoel_integral Twoel_Integral_Array[NINTS];
```

- No package-wide API for accessing integrals
- Macroconfiguration based MCSCF/GVVPT/MRCI/SCQDPT
- GVVPT2/3: Intermediate Hamilton Approach (no intruder-state problem)

# MOLCAS-UNDMOL tandem

| MOLCAS | UNDMOL | “old” branch |
| --- | --- | --- |
| | `energy.exe` | |
| | | `aoints.exe` |
| | `aoints_molcas.exe`: | |
| | Parse undmol input | |
| | Determine sym-uniq atoms | |
| `SEWARD`: | ⟵Create SEWARD input | |
| Generates integrals | | |
| `UNDMOL_INT`: | | |
| `call RdOne` | | |
| Apply DKH correction | | |
| Reorder 1e-integrals | | |
| (inserting 0-blocks) | | |
| `call RdOrd` | | `symmetry.exe` |
| Write `aoints.dat` | | |
| | ⟶`aoints_molcas.exe`: | |
| | Fill AO→SAO matrix | |
| | Assign symmetry labels to AOs | |

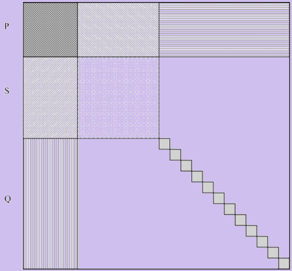
# GVVPT with Intermediate Hamiltonian approach

In the Intermediate Hamiltonian approach, we have Primary space $L_P$, secondary space $L_S$ and the external space$L_Q$. Model space is $L_P \oplus L_S$ space. The P-S interaction is considered via final single diagonalization of the model space and P-Q interaction is considered via the unitary wave operator U .

$$U = (P + Q)e^X(P + Q) \quad (1)$$

where $P$ and $Q$ are orthogonal projectors on the subspaces $L_P$ and $L_Q$, respectively, and the skew-Hermitian operator X ($X^\dagger = -X$) has the structure:

$$X = QXP - PX^\dagger Q \quad (2)$$




Hamiltonian blocks relevant to the GVVPT2 method [Fig. from :Devarajan,A.*et.al.*.,JPCA-2008, **112**(12),2677]

# GVVPT2 equations

GVVPT2 takes into account first-order perturbative effects of external configurations not only on the reference functions, but on the entire model space, and uses the following second-order approximation to the model space effective Hamiltonian matrix:

$$\mathbf{H}_{PP}^{eff} = \mathbf{H}_{PP} + \frac{1}{2}(\mathbf{H}_{PQ}\mathbf{X}_{QP} + \mathbf{X}_{PQ}^{\dagger}\mathbf{H}_{QP}) \quad (3)$$

$$\mathbf{H}_{SP}^{eff} = \mathbf{H}_{SQ}\mathbf{H}_{QP} \quad (4)$$

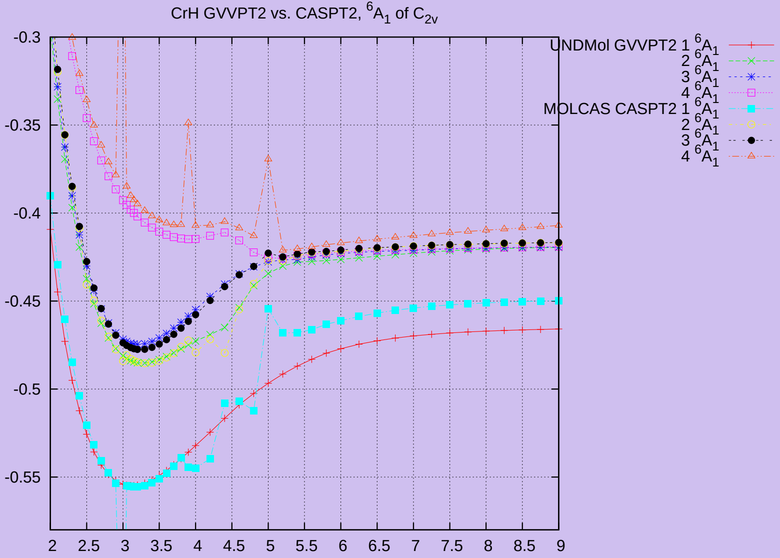
$$\mathbf{H}_{SS}^{eff} = \mathbf{H}_{SS} \quad (5)$$

$$X_{qp} = \frac{\tanh(\varepsilon_q^p - E_P')}{\varepsilon_q^p - E_P'} H_{qp} \quad (6)$$

where $\varepsilon_q^p$ is the zero-order (MP2) energy of $q$-th CSF, evaluated for a reference function $p$, $E_P'$ is the degeneracy-corrected zero-order energy of the primary state.

# CrH GVVPT2 DKH, $^6A_1$, 7/7

## Basis ANO-RCC Cr:5$s$3$p$2$d$1$f$ H:3$s$2$p$1$d$; CAS $(4a_1 1b_1 1b_2 1a_2)^7$



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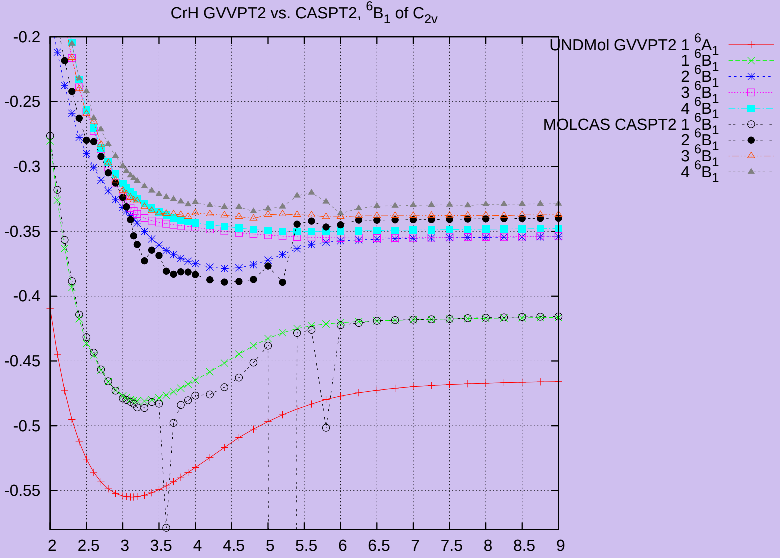

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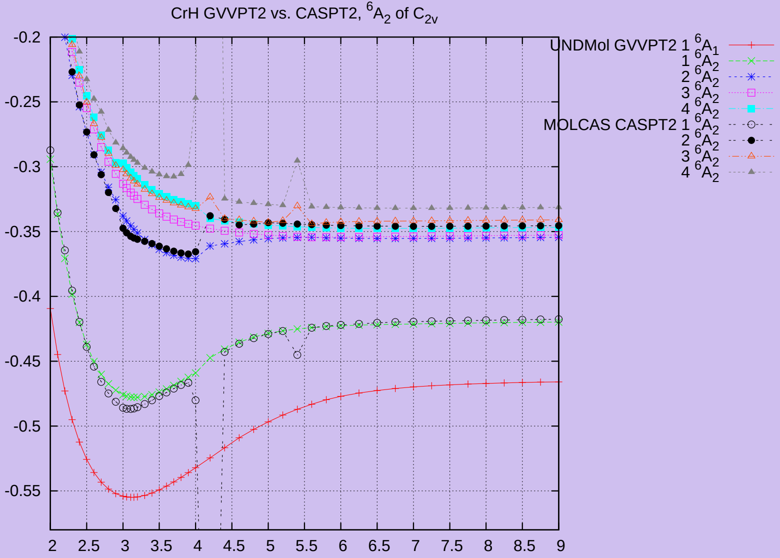

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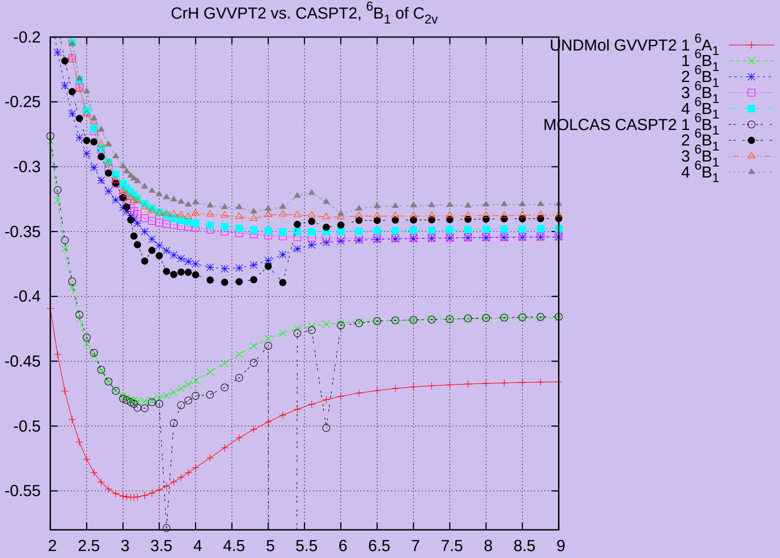
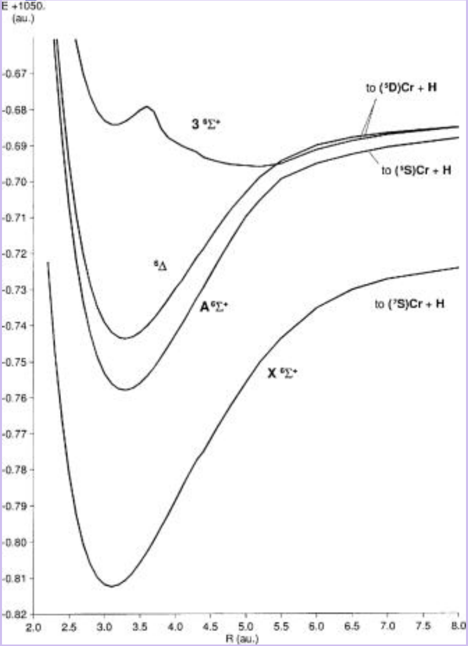


# G.Ghigo, B.O.Roos, JCP 2004, v.121(17), p.8194–8200




Cr: ANO-RCC 7*s*5*p*4*d*3*f*2*g*
H: ANO-RCC 4*s*3*p*2*d*
CAS 7/16
(5*s* & 4*p* included to avoid intruders)

# TiC GVVPT2 DKH, singlets and triplets, 8/11

Ref:
A.Kalemos,A.Mavridis//
JPCA-2002,**106**,3905

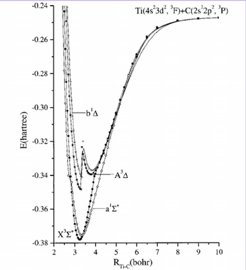
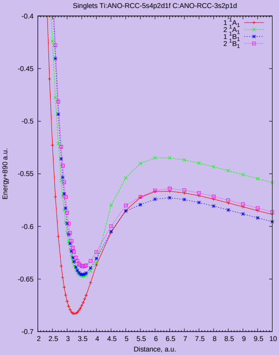
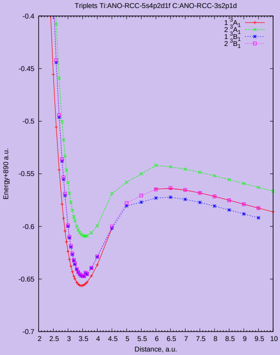



**Figure 1.** Potential energy curves of the TiC $X^3\Sigma^+$, $a^1\Sigma^+$, $A^3\Delta$, and $b^1\Delta$ states at the MRCI level. Energies have been shifted by +886.0 hartree.




ANO-RCC Ti:5s4p2d1f; C:3s2p1d;

CAS: $(6a_1 2b_1 2b_1 1a_2)^8$

The PEC is smooth, jump in the reference work is probably an artifact.

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