On the Electron Correlation Problem in Quantum Chemistry

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Outline

- Traditional and “New” Wave-Function based Correlation Methods for Strongly-Correlated Molecular Systems
- Insights from Applications in Quantum Chemistry
- Conclusions
Electronic structure theory – the Hamiltonian

- Non-relativistic many-electron Hamiltonian in position space (Hartree atomic units):

\[
H_{el} = \sum_{i}^{N} \left( -\frac{1}{2} \nabla_i^2 - \sum_{I} \frac{Z_I}{r_{iI}} \right) + \sum_{i<j}^{N} \frac{1}{r_{ij}}
\]

with \( r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \) and \( N \) being the number of electrons.

- Eigenvalue equation: electronic Schrödinger equation:

\[
H_{el} \Psi_{el}^{\{\mathbf{R}_I\}} (\{\mathbf{r}_i\}) = E_{el}(\{\mathbf{R}_I\}) \Psi_{el}^{\{\mathbf{R}_I\}} (\{\mathbf{r}_i\})
\]

- Central problem: How to approximate \( \Psi_{el} \)?
Electronic structure theory –
the two-dimensional view

On the Electron Correlation Problem in QC – Stefan Knecht
How to approximate $\Psi_{el}$?

- Construct many-electron (determinantal) basis set $\{\Phi_i\}$ from a given (finite) one-electron (orbital) basis set $\phi_i$.

- From the solution of the Roothaan–Hall equations, one obtains as $n$ orbitals from $n$ one-electron basis functions:
  \[ FC = SC\epsilon \]

- From the $N$ orbitals with the lowest energy, the Hartree–Fock (HF) Slater determinant $\Phi_0$ is constructed.

- The other determinants (configurations) are obtained by subsequent substitution of orbitals in the HF Slater determinant $\Phi_0$:
  \[
  \{\Phi_I\} \rightarrow \Phi_i^a, \Phi_j^b, \ldots \rightarrow \Phi_{ij}^{ab}, \Phi_{ik}^{ac}, \ldots \rightarrow \Phi_{ijk}^{abc}, \Phi_{ijl}^{abd}, \ldots
  \]
Electron Correlation

- Correlation energy in a given basis set as difference between the exact and the Hartree-Fock energy:
  \[ E_{corr} = E_{exact} - E_{HF} \]
- Dynamical correlation:
  - related to the movements of the individual electrons
  - short-range
- Non-dynamical or static correlation:
  - Electronic ground state as a function of many (nearly)-degenerate Slater determinants
  - Requires multi-determinantal reference wave function
Full Configuration Interaction (FCI)

- The number of possible determinants is determined by the number of virtual orbitals $n-N$
- Including all possible excited Slater determinants for a finite or infinite one-electron basis set leads to the so-called full CI approach
- Number of Slater determinants $n_{\text{SD}}$ for $N$ spin orbitals chosen from a set of $n$ spin orbitals:
  \[
  n_{\text{SD}} = \frac{n!}{N!(n-N)!}
  \]
  **Example:** There are $\approx 10^{12}$ different possibilities to distribute 21 electrons in 43 spin orbitals
- FCI only feasible for small basis sets!
Truncated CI:

- **Assumption**: Substitution hierarchy is a useful measure to generate a systematically improvable many-electron basis set.
- For example CISD:
  \[
  \Psi_{el}^{CISD} = C_0 \Phi_0 + \sum_{(ai)} C_{(ai)} \Phi_i^a + \sum_{(ai)(bj)} C_{(ai,bj)} \Phi_{ij}^{ab}
  \]

Truncated Coupled Cluster:

- Exponential ansatz
  \[
  \Psi_{el}^{CC} = \exp(T) \Phi_0
  \]
- excitation operator \( T = T_1 + T_2 + T_3 + \ldots \)
- Truncation of \( T \) defines the level of hierarchy: CCSD: \( T = T_1 + T_2 \)
- Improves on truncated CI because of inclusion of disconnected terms, CC is size-consistent \( \Rightarrow \exp(T) = 1 + T + \frac{1}{2!} T^2 + \ldots \)
Approximate Correlation Methods II

- Multi-configuration Self-Consistent-Field method (MCSCF):
  \[ \Psi_{el}^{MCSCF} = \exp(\hat{\kappa}) \left( \sum_{\nu} C_\nu \Phi_\nu \right) \]
  - Simultaneous optimization of CI coefficients and orbital rotation parameters
  - Used to generate qualitatively correct reference states for systems with quasi-degenerate electronic ground states (static correlation!)
- Most popular approach: Complete Active Space SCF (CASSCF):
  - Perform Full CI for \( n \) electrons within a set of chosen, active orbitals \( m \)
  - \( \text{CAS}(n,m) \)
The CASSCF model
Approximate Correlation Methods III

- **Truncated Multi-reference CI:**
  - Same assumptions made as in the single-reference case
  - $\Phi_0$ is replaced by a sum of reference configurations from for example a CASSCF wave function optimization

- **Multi-reference CC:**
  - Multi-reference analog of single-reference CC
  - No ultimate approach exists (yet)

- **Multi-reference Perturbation Theory (to 2nd order):**
  - For example: MP2 theory for a CAS wave function
  - Different choices of 0th-order Hamiltonian: CASPT2 or NEVPT2
Approximate Correlation Methods IV

- Density Matrix Renormalization Group (DMRG):
  - Is a CAS approach
  - DMRG state is a superposition of FCI-type basis states
  - A FCI/CAS solution can be converged; but the basis cannot be completely known if DMRG shall be efficient
  - Can be extended by orbital optimization → DMRG-SCF
  - DMRG exploits a “linear” optimization algorithm
  - See talk by Ö. Legeza for details on algorithm and MPS formulation
Methods not further mentioned here:
- Greens function approaches → ADC(X) methods
- Perturbation Theory
- Response Theory
- ...

Further reading:
Electronic structure theory – the two-dimensional view
Electronic structure theory – the Hamiltonian II

- Relativistic many-electron Hamiltonian:
  \[
  H_{el} = \sum_{i=1}^{N} \left( c\alpha_i \cdot p_i + \beta_i' mc^2 - \left( \sum_{I} \frac{Z_I}{r_{iI}} I_{4 \times 4} \right) \right) + \sum_{i<j}^{N} \hat{g}_{ij}
  \]

- 4-component wave function $\Psi_{el}$ (e+p-like solutions!)

- Two-electron interaction:
  - Coulomb: $\hat{g}_{ij} = \frac{I_{4 \times 4} \otimes I_{4 \times 4}}{r_{ij}}$
  - Coulomb-Breit: $\hat{g}_{ij} = \frac{I_{4 \times 4} \otimes I_{4 \times 4}}{r_{ij}} - \frac{1}{2r_{ij}} \left( \alpha_i \cdot \alpha_j + \frac{(\alpha_i \cdot r_{ij})(\alpha_j \cdot r_{ij})}{r_{ij}^2} \right)$
  - Higher-orders of fine structure constant $\alpha$ (QED)

- Relativity adds new axis to electronic structure problem!
Implications for choosing an appropriate QC Model

- Approximations to the “full” relativistic Hamiltonian:
  - From a four-component to a two-component (electrons only) wave function through block-diagonalization of the one-electron Hamiltonian

\[
\hat{h}_{bd} = U^\dagger \begin{bmatrix} \hat{h}_{11} & \hat{h}_{12} \\ \hat{h}_{21} & \hat{h}_{22} \end{bmatrix} U = \begin{bmatrix} \hat{h}_+ & 0 \\ 0 & \hat{h}_- \end{bmatrix}
\]

- Neglect of spin-orbit effects: scalar-relativistic approach
- Treat spin-orbit effects \textit{a posteriori} as perturbation to a scalar-relativistic correlation model

- Increase of computational cost $\rightarrow$ loss of spin symmetry
Electronic structure theory – the three-dimensional view
Further Literature On Relativistic QC

Applications
The electronic ground state of $U_2$

- $U_2$: electronic ground state is proposed to have a quintuple bond between the U atoms
  
  L. Gagliardi and B. O. Roos, Quantum chemical calculations show that the uranium molecule $U_2$ has a quintuple bond, Nature 433, 848-851 (2005).

- Scalar-relativistic CASSCF(6,20) calculations with an *a posteriori* perturbative treatment of spin-orbit coupling

- Our *ansatz*: relativistic two-component CASSCF(6,20) calculations with a variational inclusion of spin-orbit coupling → different electronic ground state and bond order of 4 for the uranium dimer!

S. Knecht et al., in preparation 2014.
The electronic ground state of $U_2$

On the Electron Correlation Problem in QC – Stefan Knecht
The electronic ground state of $U_2$

mixing of bonding and anti-bonding

classification of bonding and anti-bonding molecular orbitals:
non- and scalar-relativistic picture

\begin{align*}
\text{anti-bonding} & : \sigma_u \quad \pi_g \quad \delta_u \quad \phi_g \quad \ldots \\
\text{bonding} & : \sigma_g \quad \pi_u \quad \delta_g \quad \phi_u \quad \ldots
\end{align*}

\[ \downarrow \text{spin-orbit coupling} \]

\begin{align*}
\text{anti-bonding} & : \sigma_u \quad \pi_g \quad \delta_u \quad \phi_g \quad \ldots \\
\text{bonding} & : \sigma_g \quad \pi_u \quad \delta_g \quad \phi_u \quad \ldots
\end{align*}
The electronic ground state of $\text{U}_2$

$\Omega = 8_g$ ground state from Roos and Gagliardi

\[
\begin{align*}
7s\sigma_g^{2.00} & \quad 6d\sigma_g^{0.97} & \quad 6d\delta_g^{0.98} & \quad 5f\pi_g^{0.37} & \quad 5f\delta_g^{0.63} & \quad 5f\phi_g^{1.00} \\
6d\pi_u^{4.00} & \quad 5f\pi_u^{0.63} & \quad 5f\delta_u^{0.37} & \quad 5f\phi_u^{1.00}
\end{align*}
\]

$\Omega = 9_g$ ground state from our relativistic CASSCF calculations:

approximate scalar-relativistic notation

\[
\begin{align*}
7s\sigma_g^{1.92} & \quad 6d\sigma_g^{0.97} & \quad 6d\delta_g^{0.97} & \quad 5f\pi_g^{0.00} & \quad 5f\delta_g^{1.00} & \quad 5f\phi_g^{0.99} \\
6d\pi_u^{3.79} & \quad 5f\pi_u^{0.00} & \quad 5f\delta_u^{0.99} & \quad 5f\phi_u^{1.00}
\end{align*}
\]

$\Omega = 8_g$ state from our relativistic CASSCF calculations:

approximate scalar-relativistic notation

\[
\begin{align*}
7s\sigma_g^{1.91} & \quad 6d\sigma_g^{0.97} & \quad 6d\delta_g^{0.97} & \quad 5f\pi_g^{0.41} & \quad 5f\delta_g^{0.59} & \quad 5f\phi_g^{0.99} \\
6d\pi_u^{3.80} & \quad 5f\pi_u^{0.59} & \quad 5f\delta_u^{0.41} & \quad 5f\phi_u^{1.00}
\end{align*}
\]
Mössbauer isomer shifts in Hg complexes

- Mössbauer spectroscopy: Recoil-free, resonant nuclear absorption and emission of gamma rays in solids
- $E_\gamma$ is modified by the local chemical environment
  \[ \Delta E_\gamma \propto \Delta \rho(0) \]
  with $\rho(0)$ being the density at the nucleus
- Relativistic benchmark for the series HgF$_n$ (n=0,1,2,4)
Mössbauer isomer shifts in Hg complexes

Relativistic effects on absolute and relative $\rho^Hg(0)$ (a.u.)

<table>
<thead>
<tr>
<th>Contact density ($a_0^{-3}$):</th>
<th>absolute</th>
<th>relative to Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method Hamiltonian</td>
<td>Hg</td>
<td>HgF</td>
</tr>
<tr>
<td>HF DC</td>
<td>2363929.12</td>
<td>-114.48</td>
</tr>
<tr>
<td>HF NR</td>
<td>361818.93</td>
<td>-11.92</td>
</tr>
<tr>
<td></td>
<td>-84.69%</td>
<td>-89.59%</td>
</tr>
</tbody>
</table>
Mössbauer isomer shifts in Hg complexes

Correlation effects

<table>
<thead>
<tr>
<th>Method</th>
<th>Hamiltonian</th>
<th>Contact density ((a_0^{-3}))</th>
<th>absolute</th>
<th>relative to Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>DC</td>
<td>2363929.12</td>
<td>-114.48</td>
<td>-127.92</td>
</tr>
<tr>
<td>CCSD(T)[all]</td>
<td>DC</td>
<td>2364016.40</td>
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<td></td>
</tr>
<tr>
<td>CCSD(T)[cv]</td>
<td>DC</td>
<td>2363990.74</td>
<td>-95.11</td>
<td>-110.46</td>
</tr>
</tbody>
</table>

- Correlation effect on the absolute contact density are small but relative contact densities are of the same order
- Correlation effect on relative densities therefore important
Nuclear size effects in rotational spectra

- Molecular field shift $V^x$ arising from the finite size of the atomic nuclei as an additional correction factor to the Born-Oppenheimer approximation
  

- Requires to compute the gradient of density at the nucleus

  \[ V^x \propto \left( \frac{d\rho(0)}{dR} \right) R_e \]

- Computational benchmark for TII, PtSi and PbTe
  
Nuclear size effects in rotational spectra

Comparison of both the calculated and, where available, measured electron density gradient $\rho_{\text{HIX}}$ (in Å$^{-4}$) at the Tl, Pb, and Pt nuclei and the field shift parameter $V^X$ (in $10^4$ Å$^{-2}$). Besides our best theoretical estimates computed at the 4-component molecular mean-field CCSD(T)/TZ + 2s1p level ($4c\text{DC}^{**}$), we also list non-relativistic (NR) DFT/SAOP/TZ + 2s1p data.

<table>
<thead>
<tr>
<th>Method</th>
<th>Hamiltonian</th>
<th>$\rho_{\text{HIX}}$</th>
<th>$V^X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment[A]$^a$</td>
<td>120.6(38)</td>
<td>3.20(10)</td>
<td></td>
</tr>
<tr>
<td>Experiment[B]$^b$</td>
<td>12.06(38)</td>
<td></td>
<td></td>
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<tr>
<td>DFT/SAOP</td>
<td>NR</td>
<td>21.09</td>
<td>0.57</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>$4c\text{DC}^{**}$</td>
<td>142.26</td>
<td>3.81</td>
</tr>
<tr>
<td>DFT/SAOP</td>
<td>(ZORA)</td>
<td>21.1</td>
<td>0.61$^d$</td>
</tr>
<tr>
<td>PbTe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment$^a$</td>
<td>148(11)</td>
<td>2.12(16)</td>
<td></td>
</tr>
<tr>
<td>Experiment$^b$</td>
<td>14.8(11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DFT/SAOP</td>
<td>NR</td>
<td>19.64</td>
<td>0.28</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>$4c\text{DC}^{**}$</td>
<td>163.19</td>
<td>2.36</td>
</tr>
<tr>
<td>DFT/SAOP</td>
<td>(ZORA)</td>
<td>21.1</td>
<td>0.33$^d$</td>
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<tr>
<td>PtSi</td>
<td></td>
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<tr>
<td>experiment[C]$^a$</td>
<td></td>
<td></td>
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<tr>
<td>DFT/SAOP</td>
<td>NR</td>
<td>$-135.64$</td>
<td>$-1.14$</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>$4c\text{DC}^{**}$</td>
<td>$-599.83$</td>
<td>$-5.05$</td>
</tr>
<tr>
<td>DFT/SAOP</td>
<td>(ZORA)</td>
<td>$-136.5$</td>
<td>$-1.10$</td>
</tr>
</tbody>
</table>

$^a$ Original result published in Ref. [27] in 1982.
$^c$ Ref. [38]; a QZ4P basis set was used in the DFT calculations.
$^d$ Ref. [40].
$^e$ Ref. [39]; a QZ4P basis set was used in the DFT calculations.
Spectroscopic constants of TIH

- TIH as “guinea pig” molecule for any new relativistic correlation method
- Comparison of our new relativistic DMRG implementation with CI and CC methods
- CAS space: 14 electrons in 94 spinors

Spectroscopic constants of TIH

<table>
<thead>
<tr>
<th>Method</th>
<th>$r_e$ (Å)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$\omega_e x_e$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4c-DMRG(14,94)[512]</td>
<td>1.873</td>
<td>1411</td>
<td>26.64</td>
</tr>
<tr>
<td>4c-CISD(14,94)</td>
<td>1.856</td>
<td>1462</td>
<td>23.11</td>
</tr>
<tr>
<td>4c-CISDTQ(14,94)</td>
<td>1.871</td>
<td>1405</td>
<td>20.11</td>
</tr>
<tr>
<td>4c-MP2(14,94)</td>
<td>1.828</td>
<td>1546</td>
<td>47.27</td>
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<tr>
<td>4c-CCSD(14,94)</td>
<td>1.871</td>
<td>1405</td>
<td>19.36</td>
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<tr>
<td>4c-CCSD(T)(14,94)</td>
<td>1.873</td>
<td>1400</td>
<td>23.52</td>
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<tr>
<td>4c-CCSDT(14,94)</td>
<td>1.873</td>
<td>1398</td>
<td>22.28</td>
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<tr>
<td>4c-CCSDT(Q)(14,94)</td>
<td>1.873</td>
<td>1397</td>
<td>21.01</td>
</tr>
<tr>
<td>CCSD(T)$^a$</td>
<td>1.876</td>
<td>1385</td>
<td>n/a</td>
</tr>
<tr>
<td>CCSD(T)$^b$</td>
<td>1.877</td>
<td>1376</td>
<td>n/a</td>
</tr>
<tr>
<td>MRD-CI$^c$</td>
<td>1.870</td>
<td>1420</td>
<td>n/a</td>
</tr>
<tr>
<td>SO-MCQDPT$^d$</td>
<td>1.876</td>
<td>1391</td>
<td>29.42</td>
</tr>
<tr>
<td>Experiment$^e$</td>
<td>1.872</td>
<td>1390.7</td>
<td>22.7</td>
</tr>
</tbody>
</table>

$^a$4c-DC CCSD(T) [14 electrons], see Ref. 35.
$^b$4c-DC-Gaunt CCSD(T) [36 electrons], see Ref. 35.
$^c$GRECP spin-orbit MRD-CI, see Ref. 34.
$^d$Model-core potential spin-orbit MCQDPT, see Ref. 40.
$^e$Experimental data taken from Refs. 34 and 55–57.
Conclusions

- Electron correlation plays an important role in describing the electronic structure and properties of molecular systems.
- Relativistic effects may not be non-negligible for light systems and are mandatory for heavy-element compounds.
- Efficient and “new” wave-function based electron correlation methods are highly appreciated.
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