The Vibrational Auto-adjusting Perturbation Theory (VAPT)

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10.07.2009
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Conventions and notation

- Capital letters used for matrices, $H$, $\Phi$, $E$, ...
- Lower case for scalars and matrix elements $h_{ii}$, $\phi_{ij}$, $e_{pp}$, $e$ ...
- Bra-ket notation for vectors.
- When matrix notation used, vectors are collected in columns.
- Overline $(\overline{E}^{(k)})$ is used to denote accumulated quantities.
- Superscript brackets, $X^{(k)}$ denotes the order in the standard perturbation series.
- Superscript square brackets, $X^{[k]}$ denotes order in the APT series.
Mind that we need to solve Schrödinger Perturbation Theory

\[ H \Phi = E \Phi \]

where \( H = H^{(0)} + V^{(1)} \) and \( \Phi^{\dagger} \Phi = \Phi \Phi^{\dagger} = I \). We have a complete knowledge of the unperturbed system:

\[ H^{(0)} \Phi^{(0)} = E^{(0)} \Phi^{(0)} \]

where \( \Phi^{(0)}^{\dagger} \Phi^{(0)} = \Phi^{(0)} \Phi^{(0)}^{\dagger} = I \). Let us expand in Taylor series (each term corresponding to a correction) both the matrix \( \Phi \) and \( E \):

\[
\Phi = \sum_{i=0}^{\infty} \Phi^{(k)} \\
E = \sum_{i=0}^{\infty} E^{(k)}
\]
Rayleigh-Schrödinger Perturbation Theory in Matrix Form

Now, expanding we get:

\[ H^{(0)} \Phi + V^{(1)} \Phi = \Phi E \]

\[ H^{(0)} \sum_k \Phi^{(k)} + V^{(1)} \sum_k \Phi^{(k)} = \sum_{k,l} \Phi^{(k)} E^{(l)} \]

from which we pick up the \( n^{th} \) order term:

\[ H^{(0)} \Phi^{(n)} + V^{(1)} \Phi^{(n-1)} = \sum_p \Phi^{(n-p)} E^{(p)} \]

It is assumed the unperturbed vectors can expand the perturbed ones:

\[ \Phi = \Phi^{(0)} Z \]

and since we may write \( Z = \sum_{k}^{\infty} Z^{(k)} \) we have:

\[ \Phi^{(k)} = \Phi^{(0)} Z^{(k)} \]
At this point one may notice that we have changed the basis of representation, and generated a new eigenvalue problem, straightforwardly related with the original one:

\[
H \Phi^{(0)} Z = \Phi^{(0)} Z E
\]

\[
\left(\Phi^{(0)\dagger} H \Phi^{(0)}\right) Z = Z E
\]

\[
R^{[0]} Z = Z E
\]

\[
R^{[0]} = E^{(0)} + P^{[0]}
\]

Notice that we have an initial problem which can be summarized as follows: \( (H, H^{(0)}, V^{(1)}, \Phi^{(0)}, E^{(0)}) \) and we go to another problem which is \( (R^{[0]}, E^{(0)}, P^{[0]}, I, E^{(0)}) \).
Now we may multiply the wfn on the left side by $\Phi^{(0)\dagger}$:

$$
\Phi^{(0)\dagger} H^{(0)} \Phi^{(n)} + \Phi^{(0)\dagger} V^{(1)} \Phi^{(n-1)} = \sum_{p=0}^{n} \Phi^{(0)\dagger} \Phi^{(n-p)} E^{(p)}
$$

$$
E^{(0)} Z^{(n)} + \Phi^{(0)\dagger} V^{(1)} \Phi^{(0)} Z^{(n-1)} = Z^{(n)} E^{(0)} + \sum_{p=1}^{n} Z^{(n-p)} E^{(p)}
$$

and we can identify new matrix elements $n > 0$:

$$
Q^{(n)} = E^{(0)} Z^{(n)} - Z^{(n)} E^{(0)}
$$

$$
Q^{(n)} = -\Phi^{(0)\dagger} V^{(1)} \Phi^{(0)} Z^{(n-1)} + \sum_{p=1}^{n} Z^{(n-p)} E^{(p)}
$$

From the latter Eq. one find the relationship between $Q$ and $Z$:

$$
q_{ij}^{(n)} = e_{ii}^{(0)} z_{ij}^{(n)} - z_{ij}^{(n)} e_{jj}^{(0)}
$$

$$
z_{ij}^{(n)} = \frac{q_{ij}^{(n)}}{e_{ii}^{(0)} - e_{jj}^{(0)}}
$$
Also:

\[ E^{(n)} = \text{Diag}\{ \Phi^{(0)\dagger} V^{(1)} \Phi^{(0)} Z^{(n-1)} \} = \text{Diag}\{ P^{[0]} Z^{(n-1)} \} \]

Altogether the procedure to solve the initial eigenvalue problems follows this scheme:

1.- \( E^{(n)} = \text{Diag}\{ P^{[0]} Z^{(n-1)} \} \)

2.- \( Q^{(n)} = -P^{[0]} Z^{(n-1)} + \sum_{p=1}^{n} Z^{(n-p)} E^{(p)} \)

3.- \[ z^{(n)}_{ij} = \frac{q^{(n)}_{ij}}{e^{(0)}_{ii} - e^{(0)}_{jj}} \]

4.- \( \Phi^{(n)} = \Phi^{(0)} Z^{(n)} \)
We formulate the problem in terms of the sigma vector for a diagonal unperturbed hamiltonian $H^{(0)} = E^{(0)}$ e.g. Møller-Plesset-RSPT:

$$|\sigma^{(n)}\rangle = H|\Phi^{(n-1)}\rangle$$

We get the energy and the wavefunction correction in terms of $|\sigma^{(n)}\rangle$:

$$e^{(n)} = \langle \Phi^{(0)} | \sigma^{(n)} \rangle \quad \forall n > 1$$

$$|\Phi^{(n)}\rangle = \left( H^{(0)} - e^{(0)} \right)^{-1} \left( H^{(0)} | \Phi^{(n-1)} \rangle - |\sigma^{(n)}\rangle + \sum_{k=1}^{n} e^{(k)} |\Phi^{(n-k)}\rangle \right)$$

Notice the use of $e$ for energy of the $p^{th}$ state, while we used $E$ for the diagonal matrix containing the corrections for all states.
Auto-adjusting Perturbation Theory

Now, let’s go back again at the point where we had the vector: 
\( (R[0], E^{(0)}, P[0], I, E^{(0)}) \) and let’s assume we somehow get a correction of \( \Psi \) and \( E \):

\[
\Psi[1] = \Psi[0] + \Theta[1] \quad \overline{E}[1] = E^{(0)} + \Delta[1]
\]

we can now define the Hamiltonian of this new reference system as:

\[
H[1] = \Psi[1] \overline{E}[1] \left( \Psi[1] \right)^{-1}
\]

and so its perturbation:

\[
\]

Again, we are left with a new vector problem:

\( (R[0], H[1], V[1], \Psi[1], \overline{E}[1]) \)
The perturbation matrix can be likewise expanded in the basis of the reference system:

\[ P^{[1]} = \left( \psi^{[1]} \right)^{-1} V^{[1]} \psi^{[1]} \]

from which we can deduce

\[ R^{[0]} = \psi^{[1]} \left( \overline{E}^{[1]} + P^{[1]} \right) \left( \psi^{[1]} \right)^{-1} \]

\[ H = \psi^{[0]} \psi^{[1]} \left( \overline{E}^{[1]} + P^{[1]} \right) \left( \psi^{[1]} \right)^{-1} \left( \psi^{[0]} \right)^{-1} \]

And, yes! We are left with a new vector problem:

\( \left( R^{[1]}, \overline{E}^{[1]}, P^{[1]}, I, \overline{E}^{[1]} \right) \)
We can formulate the algorithm as a twofold iteration procedure:

\[
\psi^{[i]} = I + Z^{[1]}
\]

The matrix is diagonalized by successive application of the corrections:

\[
H = \psi^{[0]}\psi^{[1]}...\psi^{[n]} \left( E^{[n]} + P^{[n]} \right) \left( \psi^{[n]} \right)^{-1} ... \left( \psi^{[1]} \right)^{-1} \left( \psi^{[0]} \right)^{-1}
\]
The APT for a RSPT Perturbation

\[ \Psi^{[1]} = Z^{[0]} + Z^{[1]} = I + Z^{[1]} \]
\[ E^{[1]} = E^{(0)} + E^{[1]} \]

with

\[ z_{ij}^{[1]} = \frac{r_{ij}^{[0]}}{\epsilon_{jj}^{(0)} - \epsilon_{ii}^{(0)}} = \frac{[\Psi^{(0)} \dagger H \Psi^{(0)}]_{ij}}{\epsilon_{jj}^{(0)} - \epsilon_{ii}^{(0)}} \]

For the time being, we won’t assume anything about the nature of \( E^{[1]} \). We notice however, that we have free choice for both \( E^{[1]} \) and \( \Psi^{[1]} \). Both quantities are connected on the next iteration, since they are both used to define the new system.
The APT for a RSPT perturbation

We will work with one state at a time, let it be the \( p^{th} \) state:

\[
Z^{[1]} = \begin{cases}
0 & \forall i = j \\
0 & \forall j \neq p \\
\delta_{ip} & i \neq p
\end{cases}
\]

The structure of such matrix simplifies greatly the task of inversing \( \Psi^{[1]} \). By simple algebra one may prove:

\[
(I + Z^{[1]})(I - Z^{[1]}) = I - (Z^{[1]})^2 = I
\]

We can define a new unperturbed system:

\[
h^{[1]}_{ij} = e^{[1]}_{ij} + z^{[1]}_{ip} \left( e^{[1]}_{ii} - e^{[1]}_{pp} \right) \delta_{jp}
\]
The APT for a RSPT perturbation

$R^{[1]}$ is first written in terms of $R^{[0]}$:

$$
R^{[1]} = \left( I - Z^{[1]} \right) R^{[0]} \left( I + Z^{[1]} \right)
= R^{[0]} - Z^{[1]} R^{[0]} + R^{[0]} Z^{[1]} - Z^{[1]} R^{[0]} Z^{[1]}
$$

Identifying matrix elements we find:

$$
\begin{align*}
\tau_{ii}^{[1]} &= \tau_{ii}^{[0]} - z_{ip} r_{pi}^{[0]} + \left( \sum_{k \neq p} \tau_{pk}^{[0]} z_{kp}^{[1]} \right) \delta_{pi} \\
\end{align*}
$$

and substituing $\tau_{ii}^{[n]} = p_{ii}^{[n]} + \bar{e}_{ii}^{[n]}$, we find the expression for $\bar{e}^{[1]}$:

$$
\begin{align*}
\bar{e}_{ii}^{[1]} &= e_{ii}^{(0)} + p_{ii}^{[0]} - \tau_{ii}^{[1]} - z_{ip}^{[1]} p_{pi}^{[0]} & \forall i \neq p \\
\bar{e}_{pp}^{[1]} &= e_{pp}^{(0)} + p_{pp}^{[0]} - p_{pp}^{[1]} + \left[ P^{[0]} Z^{[1]} \right]_{pp}
\end{align*}
$$
The APT for a RSPT perturbation

We can find the APT $p^{th}$ energy corrected to first order:

$$
e_{[1]}^{pp} = e_{[0]}^{pp} + p_{[0]}^{pp} + \left[ P_{[0]}^{0} Z_{[1]}^{1} \right]_{pp} - p_{[1]}^{pp}$$

$$e_{\text{APT}}^{[1]} = e_{\text{RSPT}}^{[0]} + e_{\text{RSPT}}^{[1]} + e_{\text{RSPT}}^{[2]} - \text{Diag}\{P_{[1]}^{1}\}$$

$$e_{\text{APT}}^{[1]} = e_{\text{RSPT}}^{[2]} - \text{Diag}\{P_{[1]}^{1}\}$$

Now, we should recall that the structure of $E^{[1]}$ remains unspecified. This degree of freedom, leaves room for the definition of $\text{Diag}\{P_{[1]}^{1}\}$.

An obvious choice (adapted here) is to take $\text{Diag}\{P_{[1]}^{1}\} = 0$, to make $e_{\text{APT}}^{[1]} = e_{\text{RSPT}}^{[2]}$. However, other choices are possible, for instance to exploit Wigner theorem and use $\text{Diag}\{P_{[1]}^{1}\} = -e_{\text{RSPT}}^{[3]}$. 
The APT for a RSPT perturbation

Using $\Psi^{[n]} = I + Z^{[n]}$ and defining $\Psi^{[n]} = \prod_{i=1}^{n} \Psi^{[i]}$ we get:

$$\bar{\psi}_{ip}^{[n+1]} = \frac{\bar{\sigma}_{ip}^{[n-1]} - \bar{e}_{ii}^{[n]} \psi_{ip}}{\bar{e}_{pp}^{[n]} - \bar{e}_{ii}^{[n]}} \quad \forall i \neq p$$

$$\bar{e}_{pp}^{[n]} = \bar{\sigma}_{pp}^{[n]}$$

with

$$\bar{e}_{ii}^{[n]} = h_{ii} - h_{pi} \bar{\psi}_{ip}^{[n]} \quad \forall i \neq p$$

$$\bar{\sigma}_{ip}^{[n]} = \left[R_{0}^{[0]} \Psi^{[n]} \right]_{ip}$$
The APT for a RSPT perturbation. Vectorial formulation.

Summarizing, assuming $H^{(0)} = E^{(0)}$, and writing it in a vectorial form:

$$e[n] = \sum_{k=0}^{n} e[k]$$

$$\left| \Psi[n] \right\rangle = \sum_{k=0}^{n} \left| \psi[k] \right\rangle$$

$$\left| \Psi[n] \right\rangle = \left( e[n-1] - E[n-1] \right)^{-1} \left( \left| \sigma[n-1] \right\rangle - E[n-1] \left| \Psi[n-1] \right\rangle \right)$$

$$e[n] = \left\langle \psi[0] \right| \sigma[n] \left\rangle$$

with

$$e_{ii}^{[n]} = h_{ii} - h_{pi}\overline{\psi}_{ip} \quad \forall i \neq p$$

$$\left| \sigma[n] \right\rangle = H \left| \Psi[n] \right\rangle$$
The APT features

\[
|\psi[n]\rangle = \left(\bar{e}[n-1] - \bar{E}[n-1]\right)^{-1} \left(|\sigma[n-1]\rangle - \bar{E}[n-1] |\psi[n-1]\rangle\right)
\]

\[
\bar{e}_{ii}[n] = h_{ii} - h_{pi} \bar{\psi}_{ip}[n] \quad \forall i \neq p
\]

- It is easy to implement.
- Scales like RSPT (as its bottleneck is also the calculation of sigma).
- However, there is no APT $2n + 1$ rule. Thus, its cost is actually double.
- It only needs to store the last correction.
- In general it is not size-consistent.
One needs knowledge about the atomic motion close to the energy minima, i.e., part of the PES.

Vibrational calculations are done on nuclear Schrödinger Eq. where modals (describing modes) replace orbitals (describing electrons). Since modes are distinguishable, things are slightly different, but not much more... Most electronic structure methods apply as-they-are.

Nowadays, people perform VSCF, VMP or VCI (expensive!) calculations. VCC (more expensive!) is in its infancy.

A given mode combination (MC) is denoted as \([a,b,c,...]\) where \(a,b,c,...\) denote the excitation level of a given mode.

Troublesome cases occur when degeneracy, i.e. when a given MC has similar energy to another. This is commonly known as (Fermi) resonance.

We use APT to calculate vibrational anharmonic energies (VAPT).
Computational Details

- The calculations are based on those done by one of us.\(^1\)
- 2DB is a two-mode model system.
- Formaldehyde calculation are based on the QFF.
- The current method\(^2\) has been implemented in MidasCpp\(^3\) package.
- VMP and VAPT calculations are performed.

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\(^1\) Christiansen, JCP 119 5773 (2003)
\(^2\) Matito, Barroso, Besalú, Christiansen, Luis, TCA 123, 41-49 (2009)
\(^3\) MidasCpp (Molecular Interactions, Dynamics and Simulation Chemistry program package in C++) Christiansen, Hansen, Kongsted, Seidler, Toffoli, Sparta, Győrffy and Matito. University of Aarhus, Aarhus, 2008.
The two-mode model system developed by Thompson and Truhlar was designed to study Fermi resonance.\(^4\)

Uses the following hamiltonian

\[
H = -\frac{1}{2} \frac{d^2}{dq_a^2} - \frac{1}{2} \frac{d^2}{dq_b^2} + \frac{1}{2} k_a q_a^2 + \frac{1}{2} k_b q_b^2 + k_{30} q_a^3 + k_{12} q_a^1 q_b^2
\]  

Using a HO basis of 33 modals per mode for VSCF.

Correlated calculations used all modals.

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\(^4\) Thompson, Truhlar CPL 75 87 (1980)
Model VMP Møller-Plesset

![Graph showing logarithm of absolute error of the energy against correction order (n). The graph includes different correction orders represented by various line styles.]
Model VAPT Møller-Plesset

Logarithm of absolute error of the energy vs. Correction order (n)

Correction order (n)

Logarithm of absolute error of the energy

[0,0] [0,1] [0,2] [1,0] [0,3] [1,1]
Quartic Force Field for Formaldehyde

- QFF developed by Bowman and coworkers.\(^5\)
- Better QFF exist, but this one is chosen because of the known divergent character of the VMP series for some states: \([0,0,0,0,1,0], [0,0,1,0,0,1], [0,1,0,0,0,1]\).
- We collect fundamentals, chosen overtones and combinations.
- We use 7 modals as the basis set for the VSCF calculation, 4 of which were retained for correlated calculations.

\(^5\)Romanowski, Bowman, Harding, JCP 82 4155 (1985)
Formaldehyde VAPT Møllner-Plesset

APT with MP partition using [ss] matrix

Log of Abs Error in au

Correction

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10th July. Platja d’Aro

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Conclusions and prospective work

- VAPT series are not divergent for all examples given.
- Use VAPT against other diagonalization methods (Davidson, Olsen, etc.)
- VAPT has a double cost, as compared to VMP.
- Do a VAPT using as much information as we can from RSPT (play with $P^{[1]}$).
- VAPT for diagonalization of asymmetric matrices $\rightarrow$ response theory.

- The whole study in: Matito, Barroso, Besalú, Christiansen, Luis; TCA special issue 123, 41-49 (2009)