Is Watson’s “Charge-Modified” Reduced Mass Always Best for Diatomic Ions?

Robert J. Le Roy\textsuperscript{1} and Nikesh S. Dattani\textsuperscript{2}

\textsuperscript{1} Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada
\textsuperscript{2} Quantum Chemistry Laboratory, Kyoto University, Kyoto 606-8103, Japan

Research supported by the Natural Sciences and Engineering Research Council of Canada.
Traditional diatomic spectroscopic data analyses involve four steps:

1. Measure and assign the data.

2. Fit the observed transition energies to Dunham-type expressions... power series in \([J(J + 1)]\) and \((v + 1/2)\), for the upper and lower level of each transition.

3. Use the resulting expressions for \(G_v\) and \(B_v\) in an RKR calculation to obtain a pointwise potential energy function for the domain spanned by the data.

4. Use this potential energy function to calculate transition intensities, predict unobserved level and transition energies, and predict dynamical properties of the molecule.
Traditional diatomic spectroscopic data analyses involve four steps:

1. Measure and assign the data.

2. Fit the observed transition energies to Dunham-type expressions . . . power series in \([J(J + 1)]\) and \((v + 1/2)\), for the upper and lower level of each transition.

3. Use the resulting expressions for \(G_v\) and \(B_v\) in an RKR calculation to obtain a pointwise potential energy function for the domain spanned by the data.

4. Use this potential energy function to calculate transition intensities, predict unobserved level and transition energies, and predict dynamical properties of the molecule

However . . .

- The first-order semiclassical basis of step #3 means that the potential energy function lacks full quantum-mechanical accuracy.

- A pointwise potential is a clumsy way to present and promulgate a summary of what we know about a system.

- Information about Born-Oppenheimer breakdown (BOB) effects obtained in step #2 cannot readibly be utilized in steps #3 and #4
Modern Direct-Potential-Fit (DPF) spectroscopic data analyses involve only three steps:

1. Measure and assign the data.

2. Fit energies of the upper and lower levels of observed transitions directly to analytic expressions for the potential energy and BOB functions,

3. Use these potential energy and BOB functions to predict transition intensities, to predict unobserved level and transition energies, and to predict dynamical properties of the molecule.
Modern Direct-Potential-Fit (DPF) spectroscopic data analyses involve only three steps:

1. Measure and assign the data.

2. Fit energies of the upper and lower levels of observed transitions directly to analytic expressions for the potential energy and BOB functions,

3. Use these potential energy and BOB functions to predict transition intensities, to predict unobserved level and transition energies, and to predict dynamical properties of the molecule.

Advantages . . .

- Collapses old steps #2 and #3 into one.

- Provides a much more compact and easily portable way to summarize what we know about a system.

- Provides a natural and physically meaningful way of interpreting and using BOB effects.

- Yields full quantum mechanical accuracy.
At the core of the DPF procedure, for the upper \((v' J')\) and lower \((v'' J'')\) level of every transition in the data set for isotopologue \(\alpha\) of molecule A-B, we must determine its energy \(E_{v,J}^{(\alpha)}\) and eigenfunction \(\psi_{v,J}^{(\alpha)}(r)\) by solving the radial Shrödinger equation

\[
\begin{cases}
-\frac{\hbar^2}{2\mu_\alpha} \frac{d^2}{dr^2} + \left[ V_{ad}^{(1)}(r) + \Delta V_{ad}^{(\alpha)}(r) \right] \\
+ \frac{[J(J+1) - \Lambda^2] \hbar^2}{2\mu_\alpha r^2} \left[ 1 + g^{(\alpha)}(r) \right] \psi_{v,J}^{(\alpha)}(r) = E_{v,J}^{(\alpha)} \psi_{v,J}^{(\alpha)}(r)
\end{cases}
\]

in which \(V_{ad}^{(1)}(r)\) is the effective adiabatic internuclear potential for a chosen reference isotopologue (labelled \(\alpha = 1\)), and \(\mu_\alpha\) is its reduced mass.

The potential-energy and centrifugal potential BOB correction functions, \(\Delta V_{ad}^{(\alpha)}(r)\) and \(g^{(\alpha)}(r)\), respectively, each expressed as a sum of two terms, one for each atom, whose components have magnitudes inversely proportional to the masses of the specific atomic isotopes.
At the core of the DPF procedure, for the upper \((v'J')\) and lower \((v''J'')\) level of every transition in the data set for isotopologue \(\alpha\) of molecule A-B, we must determine its energy \(E_{v,J}^{(\alpha)}\) and eigenfunction \(\psi_{v,J}^{(\alpha)}(r)\) by solving the radial Shrödinger equation

\[
\left\{-\frac{\hbar^2}{2\mu_{\alpha}} \frac{d^2}{dr^2} + \left[V_{ad}^{(1)}(r) + \Delta V_{ad}^{(\alpha)}(r)\right] + \frac{[J(J + 1) - \Lambda^2]\hbar^2}{2\mu_{\alpha} r^2} \left[1 + g^{(\alpha)}(r)\right]\right\} \psi_{v,J}^{(\alpha)}(r) = E_{v,J}^{(\alpha)} \psi_{v,J}^{(\alpha)}(r)
\]

in which \(V_{ad}^{(1)}(r)\) is the effective adiabatic internuclear potential for a chosen reference isotopologue (labelled \(\alpha = 1\)), and \(\mu_{\alpha}\) is its reduced mass.

The the potential-energy and centrifugal potential BOB correction functions, \(\Delta V_{ad}^{(\alpha)}(r)\) and \(g^{(\alpha)}(r)\), respectively, each expressed as a sum of two terms, one for each atom, whose components have magnitudes inversely proportional to the masses of the specific atomic isotopes.

In a combined-isotopologue DPF data analysis, the fit determines a unique \(V_{ad}^{(1)}(r)\) function and uniquique potential-energy and centrifugal BOB radial functions for each atom, and the isotopologue-dependence is accounted for by the \(\mu_{\alpha}\) factors in Eq. (1), and the atomic isotope masses inside the BOB terms.
But for a molecular ion, what should we use for the reduced mass factors $\mu_\alpha$?

- the two-body reduced masses of the nuclei

$$\mu_{\alpha,\text{nuc}} = \frac{m_a^{(\alpha)} m_b^{(\alpha)}}{m_A^{(\alpha)} + m_B^{(\alpha)}}$$

Most appropriate from an ab initio viewpoint.
But for a molecular ion, what should we use for the reduced mass factors $\mu_{\alpha}$?

- the two-body reduced masses of the nuclei $\mu_{\alpha}^{\text{nuc},(\alpha)} = \frac{m_a^{(\alpha)} m_b^{(\alpha)}}{m_a^{(\alpha)} + m_b^{(\alpha)}}$?

  Most appropriate from an ab initio viewpoint.

- The two-body reduced masses of the neutral atoms $\mu_{\alpha}^{\text{atom},(\alpha)} = \frac{M_A^{(\alpha)} M_B^{(\alpha)}}{M_A^{(\alpha)} + M_B^{(\alpha)}}$?

  After all, the electron mass $m_e$ is so tiny . . . why would it matter?
But for a molecular ion, what should we use for the reduced mass factors $\mu_\alpha$?

- the two-body reduced masses of the nuclei $\mu_{\alpha,nuc}^{(\alpha)} = \frac{m_a^{(\alpha)} m_b^{(\alpha)}}{m_A^{(\alpha)} + m_B^{(\alpha)}}$?

  Most appropriate from an ab initio viewpoint.

- The two-body reduced masses of the neutral atoms $\mu_{\alpha,atom}^{(\alpha)} = \frac{M_A^{(\alpha)} M_B^{(\alpha)}}{M_A^{(\alpha)} + M_B^{(\alpha)}}$?

  After all, the electron mass $m_e$ is so tiny . . . why would it matter?

- The two-body reduced masses of the ‘natural’ dissociation product species $\mu_{\alpha,nat}^{(\alpha)} = \frac{(M_A^{(\alpha)} - m_e) M_B^{(\alpha)}}{(M_A^{(\alpha)} - m_e) + M_B^{(\alpha)}}$, where atom A has a lower ionization potential than atom B?

  Seems most natural for high vibrational levels whose nuclei spend most of their time at large separations.
But for a molecular ion, what should we use for the reduced mass factors $\mu_\alpha$?

- the two-body reduced masses of the nuclei $\mu_{\alpha,\text{nuc}} = \frac{m_a^{(\alpha)} m_b^{(\alpha)}}{m_a^{(\alpha)} + m_b^{(\alpha)}}$?

  Most appropriate from an ab initio viewpoint.

- The two-body reduced masses of the neutral atoms $\mu_{\alpha,\text{atom}} = \frac{M_A^{(\alpha)} M_B^{(\alpha)}}{M_A^{(\alpha)} + M_B^{(\alpha)}}$?

  After all, the electron mass $m_e$ is so tiny . . . why would it matter?

- The two-body reduced masses of the ‘natural’ dissociation product species $\mu_{\alpha,\text{nat}} = \frac{(M_A^{(\alpha)} - m_e) M_B^{(\alpha)}}{(M_A^{(\alpha)} - m_e) + M_B^{(\alpha)}}$, where atom A has a lower ionization potential than atom B?

  Seems most natural for high vibrational levels whose nuclei spend most of their time at large separations.

- Watson’s “charge-modified” reduced mass $\mu_{\alpha,\text{Wat}} = \frac{M_A^{(\alpha)} M_B^{(\alpha)}}{M_A^{(\alpha)} + M_B^{(\alpha)} - q m_e}$, where $q$ is the net charge on the ion?

  Jim Watson is really smart . . . who am I to argue?
and two other possibilities...

- The two-body reduced masses of the ‘unnatural’ dissociation product species

\[ \mu_{\alpha}^{\text{unn},(\alpha)} = \frac{M_A^{(\alpha)} (M_B^{(\alpha)} - m_e)}{M_A^{(\alpha)} + (M_B^{(\alpha)} - m_e)} \], where atom B has a higher ionization potential than atom A?

Implausible... but we should consider everything
\[ \mu_{\alpha}^{\text{unn}} = \frac{M_A^{(\alpha)} (M_B^{(\alpha)} - m_e)}{M_A^{(\alpha)} + (M_B^{(\alpha)} - m_e)}, \]

where atom B has a higher ionization potential than atom A?

Implausible ... but we should consider everything

• "half-half" reduced masses, in which loss of electron mass is shared equally by the two atoms

\[ \mu_{\alpha}^{\text{hh}} = \frac{(M_A^{(\alpha)} - \frac{m_e}{2}) (M_B^{(\alpha)} - \frac{m_e}{2})}{(M_A^{(\alpha)} - m_e/2) + (M_B^{(\alpha)} - m_e/2)}, \]

An 'ad hoc' suggestion proposed by Coxon and Hajigeorgiou for HeH⁺


**Experimental Born–Oppenheimer Potential for the \( X^1\Sigma^+ \) Ground State of HeH⁺: Comparison with the *Ab Initio* Potential**

John A. Coxon and Photos G. Hajigeorgiou

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

Received June 23, 1998
This question was first examined by Coxon and Hajigeorgiou in their combined isotopologue DPF analysis of $\text{HeH}^+$
This question was first examined by Coxon and Hajigeorgiou in their combined isotopologue DPF analysis of HeH$^+$


Eqs. [2, 3]) result mainly from the valence electrons. Since there are no inner electrons in HeH$^+$, it seemed appropriate that nuclear masses should be employed.

Despite the success of the preliminary fits, trial fits of the data set for all four isotopomers simultaneously were not at all satisfactory. The reduced standard deviation was always two or more times those of the fits for individual isotopomers, such that the residuals between fitted and measured line positions were significantly larger than the estimated accuracies. Much effort was devoted in developing various models for the $U^i(R)$ functions of Eq. [2]. Eventually, however, it was discovered that the failure to achieve a satisfactory fit derived not from an inadequate model, but rather from the use of nuclear masses for defining the reduced masses of the isotopomers. Subsequent fits using the charge-adjusted masses (27)

$$\mu_c = \frac{M_1 M_2}{M_1 + M_2 - m_e},$$

[15]

where $M_1$ and $M_2$ are atomic masses, yielded much improved values for the reduced standard deviation.
However, Coxon and Hajigeorgiou presented no numbers, and only explicitly referred to results for three of the six cases presented above.

<table>
<thead>
<tr>
<th>Reduced Mass of...</th>
<th>( \overline{dd} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He(^+) Ion with H or D atom</td>
<td>( 1.453 )</td>
</tr>
<tr>
<td>He(^{+1/2}) Ion with H(^{+1/2}) or D(^{+1/2}) Ion</td>
<td>( 1.453 )</td>
</tr>
<tr>
<td>He Atom with H(^+) or D(^+) Ion</td>
<td>( 1.458 )</td>
</tr>
<tr>
<td>Watson Definition</td>
<td>( 1.458 )</td>
</tr>
<tr>
<td>Neutral Pair</td>
<td>( 4.391 )</td>
</tr>
<tr>
<td>Reduced Mass of Nuclei</td>
<td>( 4.391 )</td>
</tr>
</tbody>
</table>
... and including the other three raises interesting questions!

Qualility of fit $\bar{dd}$ to multi-isotopologue data for HeH$^+$.

<table>
<thead>
<tr>
<th>reduced mass of ...</th>
<th>$\bar{dd}$</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>He$^+$ ion with H or D atom</td>
<td>1.441</td>
<td>‘best’</td>
</tr>
<tr>
<td>He$^{+1/2}$ ion with H$^{+1/2}$ or D$^{+1/2}$ ion</td>
<td>1.453</td>
<td>0.843</td>
</tr>
<tr>
<td>He atom with H$^+$ or D$^+$ ion</td>
<td>1.466</td>
<td>1.725</td>
</tr>
<tr>
<td>Watson definition</td>
<td>1.458</td>
<td>1.130</td>
</tr>
<tr>
<td>neutral pair</td>
<td>3.251</td>
<td>125.567</td>
</tr>
<tr>
<td>reduced mass of nuclei</td>
<td>4.391</td>
<td>235.73</td>
</tr>
</tbody>
</table>
... and including the other three raises interesting questions!

Qualility of fit $\bar{dd}$ to multi-isotopologue data for HeH$^+$. 

<table>
<thead>
<tr>
<th>reduced mass of ...</th>
<th>$\bar{dd}$</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>He$^+$ ion with H or D atom</td>
<td>1.441</td>
<td>'best'</td>
</tr>
<tr>
<td>He$^{1/2}$ ion with H$^{1/2}$ or D$^{1/2}$ ion</td>
<td>1.453</td>
<td>0.843</td>
</tr>
<tr>
<td>He atom with H$^+$ or D$^+$ ion</td>
<td>1.466</td>
<td>1.725</td>
</tr>
<tr>
<td>Watson definition</td>
<td>1.458</td>
<td>1.130</td>
</tr>
<tr>
<td>neutral pair</td>
<td>3.251</td>
<td>125.567</td>
</tr>
<tr>
<td>reduced mass of nuclei</td>
<td>4.391</td>
<td>235.73</td>
</tr>
</tbody>
</table>

... so we had better consider some more examples!
Quality of multi-isotopologue fits for BeH\(^+\), HeH\(^+\) and CH\(^+\) using five definitions of the reduced mass. ‘\(^\%\) diff’ is \(^\%\) difference from the ‘best’ value for that species.

<table>
<thead>
<tr>
<th>partners</th>
<th>reduced mass</th>
<th>HeH(^+)</th>
<th>BeH(^+)</th>
<th>CH(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>'natural' pair(^1)</td>
<td>(\mu W \left(1 - \frac{m_e}{M_A}\right))</td>
<td>1.466 1.72</td>
<td>1.0732 0.202</td>
<td>1.30144 0.002</td>
</tr>
<tr>
<td>'half-half' pair(^2)</td>
<td>(\mu W \left(1 - \frac{m_e}{2\mu_{\text{neut}}}\right))</td>
<td>1.453 0.843</td>
<td>1.0712 0.012</td>
<td>1.30356 0.164</td>
</tr>
<tr>
<td>'unnatural' pair(^3)</td>
<td>(\mu W \left(1 - \frac{m_e}{M_B}\right))</td>
<td>1.441 ‘best’</td>
<td>1.0718 0.072</td>
<td>1.30587 0.342</td>
</tr>
<tr>
<td>neutral pair</td>
<td>(\mu W \left(1 - \frac{m_e}{M_A+M_B}\right))</td>
<td>3.251 126.</td>
<td>1.0710 ‘best’</td>
<td>1.30142 ‘best’</td>
</tr>
<tr>
<td>Watson pair</td>
<td>(\mu W)</td>
<td>1.458 1.13</td>
<td>1.0718 0.072</td>
<td>1.30521 0.291</td>
</tr>
<tr>
<td>nuclear masses</td>
<td></td>
<td>4.639 236.</td>
<td>1.0786 0.702</td>
<td>1.30597 0.349</td>
</tr>
</tbody>
</table>

\(^1\) Two-body mass with *lower* I.P. atom missing one electron mass.

\(^2\) Two-body mass with *both* atoms missing half an electron mass.

\(^3\) Two-body mass with *higher* I.P. atom missing one electron mass.
Conclusions

• Coxon and Hajigeorgiou were correct to tell us in 1998

   “It appears that the definition of reduced mass for a light
   molecular ion such as HeH$^+$ is not a trivial consideration.”
Conclusions

• Coxon and Hajigeorgiou were correct to tell us in 1998
  “It appears that the definition of reduced mass for a light molecular ion such as HeH\(^+\) is not a trivial consideration.”
• reduced masses of the nuclei alway performs worst
Conclusions

• Coxon and Hajigeorgiou were correct to tell us in 1998
  “It appears that the definition of reduced mass for a light molecular ion such as HeH⁺ is not a trivial consideration.”

• reduced masses of the nuclei alway performs worst

• For 2/3 cases simple atomic reduced masses is best, but for HeH⁺ it is terrible
Conclusions

• Coxon and Hajigeorgiou were correct to tell us in 1998
  “It appears that the definition of reduced mass for a light molecular ion such as HeH$^+$ is not a trivial consideration.”

• reduced masses of the nuclei always perform worst

• For 2/3 cases simple atomic reduced masses is best, but for HeH$^+$ it is terrible

• Watson reduced masses never the best, but never far off
Conclusions

- Coxon and Hajigeorgiou were correct to tell us in 1998
  
  “It appears that the definition of reduced mass for a light molecular ion such as HeH\(^+\) is not a trivial consideration.”

- reduced masses of the nuclei always perform worst
- For 2/3 cases simple atomic reduced masses is best, but for HeH\(^+\) it is terrible
- Watson reduced masses never the best, but never far off

- **Recommendation:** for ions other than HeH\(^+\) stick with reduced masses of neutral atoms.