IS WATSON'S "CHARGE-MODIFIED" REDUCED MASS ALWAYS BEST FOR DIATOMIC IONS ?

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Watson's landmark reformulation of the Born-Oppenheimer separation problem has been the basis of most combined-isotopologue analyses of diatomic spectroscopic data since 1980.[a] One noteworthy feature of this work was his proposal that description of the dynamical behaviour of a diatomic ion with ($\pm$) charge Q, formed from atoms with isotopic masses of M_1 and M_2, should use a "charge-modified" reduced mass: $\mu_{\rm Wat} \equiv M_1\,M_2/(M_1 + M_2 - Q\,m_e)$, in which m_e is the electron mass, and this proposal seems to have been benignly accepted and adopted. The first quantitative test of this proposal was in the pioneering combined-isotopologue direct-potential-fit (CI-DPF) study of HeH^+ by Coxon and Hajigeorgiou in 1999,[b] where they compared the quality of fit for analyses that used different choices for the definition of the reduced masses of the various isotopologues, and found that the best choice seemed to be to use conventional two-body reduced masses for $\left(M_1 - \frac{1}{2}m_e\right)$ and $\left(M_2 - \frac{1}{2}\,m_e\right)$. This question was re-examined recently in the context of a CI-DPF study of CH^+, and a rather different conclusion was reached.[c] The present paper combines new CI-DPF studies of HeH^+ and BeH^+ with our recent CH^+ work, and attempts to draw some general conclusions on this matter.

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[a] J.K.G. Watson, *J. Mol. Spectrosc.* **80**, 411 (1980)

[b] J.A. Coxon and P. Hajigeorgiou, *J. Mol. Spectrosc.* **193**, 306 (1999).

[c] Y.-S. Cho and R.J. Le Roy, *J. Chem. Phys.* **144**, 024311 (2016).