Title:	Diagonal Born–Oppenheimer correction for coupled-cluster wave-functions
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Abstract:	We examine how geometry-dependent normalisation freedom of electronic wave-functions affects extraction of a meaningful diagonal Born–Oppenheimer correction (DBOC) to the ground-state Born–Oppenheimer potential energy surface (PES). By viewing this freedom as a kind of gauge-freedom, it is shown that DBOC and the resulting associated mass-dependent adiabatic PES are gauge-invariant quantities. A sum-over-states (SOS) formula for DBOC which explicitly exhibits this invariance is derived. A biorthogonal formulation suitable for DBOC computations using standard unnormalised coupled-cluster (CC) wave-functions is presented. This is shown to lead to a biorthogonal version of SOS formula with similar properties. On this basis, different computational schemes for evaluating DBOC using approximate CC wave-functions are derived. One of this agrees with the formula used in the current literature. The connection to adiabatic-to-diabatic transformations in non-adiabatic dynamics is explored and complications arising from biorthogonal nature of CC theory are identified.
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