EXACT DIATOMIC POTENTIALS FROM DIRECT FITTING: A NEW APPROACH

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About 40 years ago, computational diatomic spectroscopy got a great boost when the RKR method was (1) rendered computationally tractable through the advent of computers and clever algorithms, and (2) found to yield potentials that were remarkably reliable for quantum mechanical purposes, in spite of its semiclassical origin. Over the years improvements have been made in both theoretical and computational aspects of the RKR method. However, in the last 15 years or so, attention has turned more toward the direct determination, through least-squares fitting, of quantum mechanically reliable diatomic potentials.

One of the drawbacks to many methods in use is the production of physically unreal potentials outside the region of internuclear distance $R$ that is sampled by the experimental data. The present paper discusses an approach that avoids this problem. Quantum mechanical wavefunctions to a starting potential (RKR or other) are taken as the basis functions for the corrections to the potential. By definition, the corrections are thus confined to the ”business” region; and the fitting is facilitated by the near-orthogonality of the basis set. One drawback: The final potentials are rendered in numerically tabulated form (like RKR curves) rather than in closed form.