

# Convergence of the Corrected Polarization/Symmetrized Rayleigh-Schrödinger Perturbation Theory

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The original Polarization/Symmetrized Rayleigh-Schrödinger (SRS) theory neither converges nor provides a unique connection between the unperturbed state and the physical ground state for systems containing atoms of atomic number 3 or greater.<sup>1</sup> Thus, there is no fundamental reason for the SRS theory to work as well as it does. The corrected SRS theory (cSRS) was designed to be free of the defects of the original.<sup>2</sup> It includes a short range potential which, order by order, makes small contributions to the expansion. Their cumulative effect, however, can make the expansion converge. The potential is included in a way that does not change the physical energies. Calculations on LiH have shown the cSRS theory converges for certain choices of the potential.<sup>3</sup> To better understand the cSRS theory we have calculated convergence radii for He<sub>2</sub>, LiH and Li<sub>2</sub> in the configuration interaction (CI) approximation at finite and infinite nuclear separations using three short range potentials. This was done by solving the eigenproblem that is the starting point for the perturbation theory. It requires that we calculate electronic wave functions which have no special symmetry under the interchange of electronic coordinates between atoms. The functions are antisymmetric only under the interchange of coordinates belonging to the same atom. Although the calculations were done on a limited number of systems it is possible to draw some general conclusions about the properties of the cSRS theory and its limitations. The conclusions are based on our understanding of the physical effect of the short range potential and our understanding of the nature of the wave functions that determine the convergence radii.

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<sup>1</sup> W. H. Adams, *Int. J. Quantum Chem.* **60**, 273(1996).

<sup>2</sup> W. H. Adams, *Theor. Chem. Acc.* **108**, 225 (2002).

<sup>3</sup> K. Patkowski, B. Jeziorski, and K. Szalewicz, *J. Chem. Phys.* **120**, 6849 (2004).