

# New *ab initio* approaches for accurate description of the bond breaking processes

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Standard *ab initio* approaches that are based on the single-reference function often encounter difficulties along the reaction paths. To improve this situation several new developments are presented.

One approach is represented by the recently invented method, correlation energy extrapolation by intrinsic scaling (CEEIS) [1] where the near-spectroscopic accuracy along the dissociation path can be achieved. Most recently, the CEEIS method has been used for the accurate calculation of the potential energy curve of the oxygen molecule [2,3] in the ground state  $^3\Sigma_g^-$  at the CBS limit with the additional corrections due to the core-correlation and relativity. The *ab initio* rotational-vibrational levels ( $v = 0-35$ ) in  $O_2$  have been found to be within  $12.8\text{ cm}^{-1}$  of the available experimental values. Furthermore, the additional (so far unobserved) rotational-vibrational levels are predicted from *ab initio* theory from  $v=36$  to  $v=41$  [3], thus offering a challenge for the experimentalists.

The second approach has to do with reducing the amount of “configurational deadwood” in configuration interaction (CI) wavefunctions to afford the exploration of larger systems. Several avenues are explored that are capable of generating very compact CI expansions. The physical insights regarding the shapes of the long-range potentials in the symmetric dissociation of  $F_2$  [4] and  $CO_2$  [5] molecules are also presented.

[1] L. Bytautas, K. Ruedenberg, *J. Chem. Phys.* **121**, 10905 (2004).

[2] L. Bytautas, K. Ruedenberg, *J. Chem. Phys.* **132**, 074109 (2010).

[3] L. Bytautas, N. Matsunaga, K. Ruedenberg, *J. Chem. Phys.* **132**, 074307 (2010).

[4] L. Bytautas, K. Ruedenberg, *J. Chem. Phys.* **130**, 204101 (2009).

[5] L. Bytautas, G. E. Scuseria (in preparation).