Approximate lower bounds via Löwdin's bracketing function

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In quantum chemistry the usage of upper bounds to the energy is well spread. In contrast to upper bounds, lower bounds are barely used, because they are much more complicated and can only be applied if appropriate conditions are fulfilled.

Löwdin's bracketing function[1], $f(\varepsilon)$ gives a lower bound if the argument ε is an appropriate upper bound. In general the argument and the value of the function „brackets" at least one eigenvalue. Taking a normalised reference function φ, the bracketing function is expressed as:

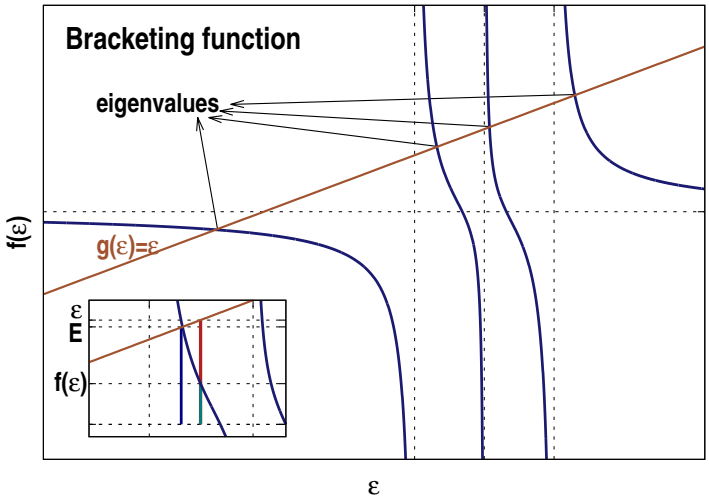
$$f(\varepsilon) = \langle\varphi|H + H\frac{P}{\varepsilon - H}H|\varphi\rangle, \qquad P = 1 - |\varphi\rangle\langle\varphi|.$$

The bracketing function can be written almost everywhere in the alternative form:

$$f(\varepsilon) = \langle\varphi|H|\varphi\rangle + \langle\varphi|(H-\varepsilon)^{-1}|\varphi\rangle^{-1}$$

Calculation of the lower bound is computionally demanding due to the operator inverse. To explore practical approaches we used several numerical approximations. The approximate formulae are evaluated at each step of a Davidson full CI iteration sequence on the example of simple molecules. An interesting result is that approximations based on the latter formula are less sensitive to the choice of the upper bound than the former.

Based on a variational principle which holds for this lower bound we studied constrained optimization of the reference function by maximizing the lower bound. We showed that solving the linearised simultaneous equations for the wave function, the nonsymmetric formula results the CEPA0 energy.



[1] Per-Olov Löwdin *Phys. Rev.*, 139:A357-A372, 1965.