

Löwdin's bracketing function revisited

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Abstract A variational principle is formulated for Löwdin's bracketing function. Setting the bracketing function stationary leads to the eigenvalue equation of the resolvent operator. An Eckart-type inequality is derived for the wavefunction optimized this way. A linearized approximation of the resolvent eigenvalue equation – reminiscent of the simplest coupled electron pair (CEPA0) treatment – is examined. We prove that the asymmetric energy formula of the resulting approximate function is a strict lower bound.

Keywords lower bound · bracketing function · variation principle · resolvent · Eckart inequality · CEPA0

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1 Introduction

Bound states of quantum systems are nowadays routinely computed by quantum chemical approximation methods. An important principle underlying a class of these techniques – the so-called variational methods – is the equivalence of the Schrödinger-equation and the minimization of the Rayleigh-quotient, serving as upper bound. Lower bounds, in comparison, play no such distinguished role.

In fact, lower bounds are not as easily accessible as the Rayleigh-quotient. One of the difficulties hindering widespread application is that the bounding property is often subject to some condition. A further discouraging observation is that lower bounds are computationally more involved than the expectation value of H , with e.g. H^2 or H^{-1} appearing.

Löwdin's bracketing function[1], $f(\varepsilon)$ ¹

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

provides an example for the features mentioned. It gives e.g. a lower bound to the ground state eigenvalue of H , if the argument ε satisfies

$$E_0 < \varepsilon < {}^P E_0 . \quad (2)$$

In the above φ is the normalized reference function, E_0 is the ground state energy while ${}^P E_0$ is the lowest eigenvalue of PHP , with

$$P = I - |\varphi\rangle\langle\varphi| ,$$

and

$$O = |\varphi\rangle\langle\varphi| .$$

Tightness of $f(\varepsilon)$ depends on two factors: (i) tightness of the upper bound, ε and (ii) the derivative of the function evaluated at the exact eigenvalue, $f'(E_0)$. Direct application of the bracketing function is scarce, as the expression involves the inverse of $P(\varepsilon - H)P$, making it computationally difficult or even impractical.

Approximations of the bracketing function often rely on a perturbative partitioning, i.e. $H = H^{(0)} + V$, which allows to write $f(\varepsilon)$ as

$$f(\varepsilon) = E^{(0)} + \langle \varphi | V + V \frac{P}{\varepsilon - H} V | \varphi \rangle = E^{(0)} + \langle \varphi | t | \varphi \rangle ,$$

provided that $H^{(0)}|\varphi\rangle = E^{(0)}|\varphi\rangle$. It is usual to apply Bazley's inner projection[2,3] to the reaction operator, t above[4,5], an estimation ensuring strict lower bound at the cost of the further condition that t is positive. Lower bounds based on inner projection have been studied extensively, using model systems for which positivity of t can be easily ensured[6,7]. While the Hamiltonian of molecular systems does not offer a trivial splitting for $H^{(0)}$ and V leading to a positive reaction operator, one may envisage tuning the partitioning by level shifts[8], to achieve it. Unfortunately, such a treatment may interfere unfavorably with the tightness of the approximation, according to our experience. The bracketing function is not in the forefront of current quantum chemistry, though it has been found implicit in coupled cluster approaches based on the method of moments[9].

The long-term goal of our studies on lower bounds is to devise approximations based on the bracketing function, without applying inner projection. At the present stage we formulate and prove some theorems which – in our view – represent good ground for further investigations. First we show a variational property of the bracketing function, setting an analogy with the

¹ Notation $\frac{P}{\varepsilon - H}$ is a shorthand for the reduced resolvent, defined correctly as $P(\alpha O + P(\varepsilon - H)P)^{-1}P$, with scalar $\alpha \neq 0$ [1].

Rayleigh-quotient. A linear variational procedure is devised then to determine the wavefunction based on the stationary condition. Linearization of the equations leads to an expression showing analogy with the simplest coupled electron pair (CEPA0)[10,11] wavefunction, with the resolvent (or Green's function) substituted for the Hamiltonian. We find that the asymmetric energy formula calculated with this wavefunction is equivalent to the bracketing function of the reference φ , if no truncation is applied to the projector P .

2 Löwdin's bracketing function

Taking a normalized reference function, φ the function $f(\varepsilon)$ of Eq.(1) has the following properties[1]

- E_i is an exact eigenvalue of H if, and only if $f(E_i) = E_i$;
- $f(\varepsilon)$ has simple poles at the eigenvalues of PHP ;
- $f(\varepsilon)$ is monotonically decreasing in each sector (sectors are intervals defined by the neighboring eigenvalues of PHP).

It follows from McDonald's theorem[12] that there is strictly one eigenvalue, E_i in each sector. As a consequence of the above, considering ε an upper bound to E_i in a given sector, $f(\varepsilon)$ is a lower bound to E_i , and vice versa, justifying terminology. For example, by the condition of Eq.(2) ε is an upper bound to E_0 , lying in the bottom-most sector, $f(\varepsilon)$ is therefore a lower bound to E_0 . The bracketing property of $f(\varepsilon)$ is illustrated in Fig.1.

There exists an alternative form of $f(\varepsilon)$ [1], given by the formula

$$f(\varepsilon) = \varepsilon + \langle \varphi | G | \varphi \rangle^{-1} \quad (3)$$

with G standing for the resolvent

$$G = (H - \varepsilon)^{-1} .$$

Let us note here, that the pole structure of $f(\varepsilon)$ is not obvious to see based on form (3). On one hand, appearance of G may give the impression that discontinuities would appear at the eigenvalues of H , i.e. at $\varepsilon = E_i$. To see that this is not the case, one may expand φ in terms of the exact eigenstates of H , denoted by Ψ_i . Provided that $\langle \Psi_i | \varphi \rangle \neq 0$, the limit of the second term on the right hand side of Eq.(3) is zero, giving $f(\varepsilon) \rightarrow E_i$ as $\varepsilon \rightarrow E_i$. On the other hand, $f(\varepsilon)$ having poles at the eigenvalues of PHP is not apparent from Eq.(3). To make it obvious, the expectation value of the inverse operator $(H - \varepsilon)^{-1}$ can be expressed with the determinant of its matrix representation \mathbf{H} and a minor to give

$$\langle \varphi | G | \varphi \rangle^{-1} = \frac{\det(\mathbf{H} - \mathbf{I}\varepsilon)}{\det(\mathbf{PHP} - \mathbf{P}\varepsilon)} ,$$

with \mathbf{I} being the unit matrix and \mathbf{P} the same in space P . The expression above shows clearly the zero denominator at the eigenvalues of \mathbf{PHP} .

It is expression (3) of the bracketing function, which is found useful for proving that the stationary condition of $f(\varepsilon)$ is equivalent to the Schrödinger-equation.

2.1 Variational principle for $f(\varepsilon)$

The bracketing function, considered as a functional of the normalized reference function φ , is stationary if and only if φ is an exact eigenfunction of H . The corresponding eigenvalue is $f(\varepsilon)$. In formulae:

$$\delta f(\varepsilon) = 0 \iff H|\varphi\rangle = E|\varphi\rangle ,$$

with $E = f(\varepsilon)$.

To prove the statement, let us formulate a Lagrangian by adding to $f(\varepsilon)$ the normalization condition, supplied with multiplier λ :

$$L = \varepsilon + \langle\varphi|G|\varphi\rangle^{-1} - \lambda(1 - \langle\varphi|\varphi\rangle) .$$

Performing the variation one obtains

$$\delta L = - \langle\varphi|G|\varphi\rangle^{-2} \langle\delta\varphi|G|\varphi\rangle + \lambda \langle\delta\varphi|\varphi\rangle + c.c. .$$

Since $\delta\varphi$ is arbitrary, the condition $\delta L = 0$ leads to

$$G|\varphi\rangle \langle\varphi|G|\varphi\rangle^{-2} = \lambda|\varphi\rangle , \quad (4)$$

the eigenvalue equation of G , with $\lambda\langle\varphi|G|\varphi\rangle^2$ being the eigenvalue. Multiplying Eq.(4) by φ from the left and integrating, the multiplier is found to be

$$\lambda = \langle\varphi|G|\varphi\rangle^{-1} ,$$

yielding $\langle\varphi|G|\varphi\rangle$ for the eigenvalue. Substituting λ in Eq.(4), the equation can be written as

$$G|\varphi\rangle \langle\varphi|G|\varphi\rangle^{-1} = |\varphi\rangle .$$

Multiplying the above by G^{-1} gives

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

which can be rearranged to

$$E|\varphi\rangle = H|\varphi\rangle$$

with

$$E = \varepsilon + \langle\varphi|G|\varphi\rangle^{-1} . \quad (5)$$

Comparison with Eq.(3) reveals, that the eigenvalue is duly $f(\varepsilon)$. Q.E.D.

It is interesting to observe, that variation of $f(\varepsilon)$ leads to the eigenvalue equation of G which is obviously equivalent to the eigenvalue equation of H . Once φ is an exact eigenfunction, ε drops from expression (5) of $f(\varepsilon)$. Inspection of Eq.(1) also shows that as φ tends to an exact eigenfunction, $f(\varepsilon)$

gradually becomes the constant function $\langle \varphi | H | \varphi \rangle$, with only one profitable intersection with the identity function.²

The variational principle, together with the bracketing property of $f(\varepsilon)$ offers a way to search an eigenfunction of H by setting $f(\varepsilon)$ stationary with respect to φ . The approach is analogous to upper bound (c.f. Rayleigh-quotient) based variational methods. At difference with upper bound minimization, here appears a scalar ε which can be used for root control. Setting $\delta f(\varepsilon) = 0$ is expected to result that eigenfunction, which corresponds to the eigenvalue lying in the same sector as ε . In general, ε may estimate the eigenvalue in its own sector from above or from below. The stationary condition for $f(\varepsilon)$ implies lower bound maximization in the former case and upper bound minimization in the latter.

At this point it becomes apparent that the inverse method of Scrinzi[13], is related to Löwdin's bracketing function. Scrinzi's approach can be considered a special case of setting $\delta f = 0$, with a distinct choice for the reference function $\varphi = (H - \varepsilon)\psi$, to get rid of the operator inverse. The inverse method has been shown in turn to be closely related to Temple's lower bound[14], and equivalent to the generalized variance method[15]. Consequently, the bracketing function shows relation to all three of these lower-bound techniques.

2.2 Variation in a subspace

Apart from tuning the value of ε , roots can also be controlled by performing variation in a subspace. To obtain the corresponding equation, we formulate a projector

$$X = \sum_i^l |\Psi_i\rangle \langle \Psi_i|$$

collecting those eigenfunctions of H – denoted by Ψ_i – which we wish to omit from φ . The projector complementary to X is denoted by Y

$$Y = I - X .$$

We assume that the reference function lies in subspace Y

$$Y |\varphi\rangle = |\varphi\rangle , \tag{6}$$

and restrict variations to φ so that $\delta\varphi$ remains in subspace Y

$$Y |\delta\varphi\rangle = |\delta\varphi\rangle .$$

It appears practical here to work with the form of the bracketing function, where the norm of φ is explicitly introduced:

$$f(\varepsilon) = \varepsilon + \langle \varphi | G | \varphi \rangle^{-1} \langle \varphi | \varphi \rangle . \tag{7}$$

² In the limit where φ becomes exact, all other intersections occur exactly at the singular points of $f(\varepsilon)$, c.f. Eq.(1).

Variation of $f(\varepsilon)$ above leads to

$$\langle \delta\varphi | (-G\langle\varphi|G|\varphi\rangle^{-1}\langle\varphi|\varphi\rangle + 1) |\varphi\rangle = 0 .$$

Since $\delta\varphi$ is arbitrary but lying in Y , we can write

$$YGY |\varphi\rangle\langle\varphi|YGY|\varphi\rangle^{-1}\langle\varphi|\varphi\rangle = |\varphi\rangle , \quad (8)$$

where Eq.(6) has also been used. In parallel with the previous section, Eq.(8) is the eigenvalue equation of the resolvent reduced to space Y . To relate Eq.(8) to an equation containing H reduced to space Y , let us multiply with $(YGY)^{-1}$ to get

$$\langle\varphi|YGY|\varphi\rangle^{-1}\langle\varphi|\varphi\rangle |\varphi\rangle = (YGY)^{-1} |\varphi\rangle .$$

Projector Y corresponding to eigenfunctions of H , the inverse of YGY (in subspace Y) can be written as

$$(YGY)^{-1} = Y(H - \varepsilon)Y , \quad (9)$$

leading to

$${}^Y E |\varphi\rangle = YHY |\varphi\rangle$$

with

$${}^Y E = \varepsilon + \langle\varphi|YGY|\varphi\rangle^{-1}\langle\varphi|\varphi\rangle . \quad (10)$$

We see, that the eigenvalue equation of YHY is equivalent to the eigenvalue equation of YGY , provided that Y corresponds to exact eigenstates. For complicated systems, exact solutions are hardly available to form projector X . It is therefore of practical interest to examine what happens if X is built with approximate eigenstates of H . In such circumstances the stationary condition leads to the eigenvalue equation of the reduced resolvent, or equivalently, that of $(YGY)^{-1}$. Relation (9) however becomes invalid. Consequently, the eigenvalue problem of YHY and YGY can not be expected equivalent, when Y and H do not commute.

It is important to note at the same time, that the eigenvalue equation of YGY yields a strict lower bound – the formula of Eq.(10) – even if X is build with approximate eigenstates. This originates from the inequality $\langle\varphi|G|\varphi\rangle \leq \langle\varphi|YGY|\varphi\rangle$, which leads to ${}^Y E$ of Eq.(10) estimating E of Eq.(5) from below.

2.3 Eckart-like inequality

Once an energy is set stationary as a function of the parameters of a wavefunction Ansatz, one may ask about the quality of the optimized wavefunction. In this context, the Eckart condition[16] is cited most often, which involves the overlap

$$S = \langle \Psi_0 | \varphi \rangle ,$$

computed with the exact wavefunction, Ψ_0 . Eckart estimates $|S|^2$ from below, using the expectation value (i.e. the upper bound) and the two lowest roots of H . An analogous estimate for $|S|^2$, using the bracketing function (i.e. the lower bound) can be obtained as follows.

Let us focus on the ground state eigenfunction, and assume that ε lies in the bottom-most sector of the bracketing function. Writing the expansion of the reference function on the basis of the orthonormal eigenfunctions of H as

$$\varphi = S |\Psi_0\rangle + \sum_{i \neq 0} c_i |\Psi_i\rangle ,$$

the bracketing function of Eq.(3) can be expressed as

$$f(\varepsilon) = \varepsilon + \left(|S|^2 \frac{1}{E_0 - \varepsilon} + \sum_{i \neq 0} |c_i|^2 \frac{1}{E_i - \varepsilon} \right)^{-1} .$$

Assuming the exact eigenvalues energy ordered, i.e. $E_0 \leq E_1 \leq \dots$, the estimation

$$\frac{1}{E_i - \varepsilon} \leq \frac{1}{E_1 - \varepsilon} \quad \text{for } i \geq 2$$

holds, since $\varepsilon < E_1$. Using normalization of φ , written in the form

$$1 - |S|^2 = \sum_{i \neq 0} |c_i|^2 ,$$

the bracketing function can be estimated from below as

$$f(\varepsilon) \geq \varepsilon + \left(|S|^2 \frac{1}{E_0 - \varepsilon} + (1 - |S|^2) \frac{1}{E_1 - \varepsilon} \right)^{-1} .$$

Let us perform now the rearrangement

$$f(\varepsilon) - \varepsilon \geq \left(|S|^2 \frac{1}{E_0 - \varepsilon} + (1 - |S|^2) \frac{1}{E_1 - \varepsilon} \right)^{-1}$$

and consider two cases, based on the ordering of E_0 and ε . If ε conforms with Eq.(2), the difference $f(\varepsilon) - \varepsilon$ is necessarily negative. If on the other hand

$\varepsilon < E_0$, $f(\varepsilon) - \varepsilon$ is positive and the same holds for the right hand side of the above inequality. Both cases allow therefore to write

$$(f(\varepsilon) - \varepsilon)^{-1} \leq |S|^2 \frac{1}{E_0 - \varepsilon} + (1 - |S|^2) \frac{1}{E_1 - \varepsilon} .$$

Simplification of the above results the Eckart-like inequality

$$\frac{(E_0 - \varepsilon)(E_1 - f(\varepsilon))}{(f(\varepsilon) - \varepsilon)(E_1 - E_0)} \leq |S|^2 . \quad (11)$$

Since both φ and Ψ_0 are normalized, $1 \leq |S|^2$, and $|S|^2$ becomes 1 when φ coincides with Ψ_0 . The significance of Eq.(11) is, that φ becomes exact (i.e. $|S|^2 \rightarrow 1$) as $f(\varepsilon)$ is set stationary (hence $f(\varepsilon) \rightarrow E_0$).

3 An approximate linear variational procedure

As seen in Section 2, a stationary condition for the bracketing function leads to the eigenvalue equation of the resolvent, G . Presently we consider φ a normalized approximate function and wish to derive a correction to it, based on the stationary condition of $f(\varepsilon)$. For this end, we take an orthonormal basis $\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$ and assume that $\varphi = \varphi_0$.³ Basis functions φ_i , $i > 0$ are often called excited function, a terminology we adopt.

We wish to find coefficients c_i in the linear parametrization of the wavefunction

$$|\Phi\rangle = |\varphi\rangle + \sum_{i \neq 0} c_i |\varphi_i\rangle . \quad (12)$$

Substituting Ansatz (12) into

$$G |\Phi\rangle = |\Phi\rangle \langle \Phi | G | \Phi \rangle ,$$

the expectation value of G is readily found by projection with $\langle \varphi_0 |$

$$G_{00} + \sum_{i \neq 0} G_{0i} c_i = \langle \Phi | G | \Phi \rangle , \quad (13)$$

with the notation $G_{ij} = \langle \varphi_i | G | \varphi_j \rangle$ for matrix elements.

Coefficients c_i can be determined by projection with excited functions $\langle \varphi_j |$. Performing a linearization one arrives at the equation

$$\sum_{i \neq 0} (G_{ji} - \delta_{ij} G_{00}) c_i = -G_{j0} , \quad (14)$$

³ An orthonormal basis with φ being one of the basis vectors may not present itself right away. This is the case e.g. when φ is a so-called multideterminantal function. However, it is always possible to construct an orthonormal and complementary set to φ with an appropriate orthogonalization procedure[17, 18].

which can be solved by inverting $({}^P\mathbf{G} - G_{00}\mathbf{P})$ with ${}^P\mathbf{G}$ being the matrix of G in the space of excited functions (i.e. built of G_{ij} , $i, j > 0$) and δ_{ij} being the elements of \mathbf{P} , again with $i, j > 0$.

Equations (14) and (13) represent the working formulae of an approximate linear variational procedure, reminiscent of the simplest coupled electron pair approximation, CEPA0[10,11] of many-body theory. As CEPA0 applies to the Schrödinger-equation, matrix elements of H appear where those of G stand above. Besides being parallel, an important difference between the above equations and CEPA0 concerns the space spanned by excited functions. In the original, so-called single reference, formulation of CEPA0, φ is the Hartree-Fock determinant and φ_i , $i > 0$ are restricted to determinants directly interacting with φ via H , i.e. doubly excited.⁴ No such restriction is applied above, since nothing can be said in general of the second quantized particle rank of operator G .

Function Φ of Eq.(12) is not normalized to 1, hence $\langle\Phi|G|\Phi\rangle$ computed according to Eq.(13) is to be substituted to Eq.(7) to get an approximate lower bound to E_0 . Having linearized the coefficient equation, $f(\varepsilon)$ computed this way is not necessarily a lower bound even if ε fulfills Eq.(2).

Besides expressing the energy with G and Φ , one may think of bringing H into play also. Interestingly, the asymmetric energy formula

$$E_{as} = \langle\varphi|H|\Phi\rangle$$

does give a strict lower bound with the choice $\varepsilon = H_{00} < {}^PE_0$. To see this, let us introduce a partitioning of matrices of G and $H - \varepsilon$, defined by projectors O and P

$$\mathbf{G} \begin{pmatrix} G_{00} & \mathbf{g} \\ \mathbf{g}^\dagger & {}^P\mathbf{G} \end{pmatrix},$$

and

$$(\mathbf{H} - \varepsilon\mathbf{I}) \begin{pmatrix} 0 & \mathbf{h} \\ \mathbf{h}^\dagger & ({}^P\mathbf{H} - \varepsilon\mathbf{P}) \end{pmatrix},$$

where ${}^P\mathbf{G}$ and ${}^P\mathbf{H}$ stand for the matrix representation in the space of excited functions and elements of vectors \mathbf{g} and \mathbf{h} are G_{i0} and H_{i0} , respectively, with $i > 0$.

With the notation above, the column vector of coefficients c_i can be expressed as

$$\mathbf{c}^\dagger = - ({}^P\mathbf{G} - G_{00}\mathbf{P})^{-1} \mathbf{g}^\dagger,$$

based on Eq.(14). The asymmetric energy formula reads

$$E_{as} = \varepsilon + \mathbf{h}\mathbf{c}^\dagger = \varepsilon - \mathbf{h} ({}^P\mathbf{G} - G_{00}\mathbf{P})^{-1} \mathbf{g}^\dagger, \quad (15)$$

⁴ Restriction of the space of excited functions is an important characteristic of CEPA0, which on one hand makes it applicable in practice. On the other hand it sets a difference with Eq.(1). In particular, P in Eq.(1) must be restricted to doubles to arrive at the CEPA0 energy formula.

while $f(\varepsilon)$, expressed with φ , takes the form

$$f(\varepsilon) = \varepsilon + G_{00}^{-1}, \quad (16)$$

noting that $G_{00} = \langle \varphi | G | \varphi \rangle$. From $(\mathbf{H} - \varepsilon \mathbf{I})\mathbf{G} = \mathbf{I}$ follow the equations

$$\mathbf{h}^P \mathbf{G} = 0 \quad (17)$$

and

$$\mathbf{h} \mathbf{g}^\dagger = 1. \quad (18)$$

Adding $-\mathbf{h}G_{00}\mathbf{P}$ to Eq.(17) we get

$$\mathbf{h} ({}^P\mathbf{G} - G_{00}\mathbf{P}) = -\mathbf{h}G_{00}\mathbf{P}$$

an eigenvalue equation for \mathbf{h} in space P . Vector \mathbf{h} is eigenvector to the inverse matrix also, with the eigenvalue inverted:

$$\mathbf{h} ({}^P\mathbf{G} - G_{00}\mathbf{P})^{-1} = -\mathbf{h}G_{00}^{-1}\mathbf{P}.$$

Multiplying the above with $-\mathbf{g}^\dagger$ from the right, and using Eq.(18), we find

$$-\mathbf{h} ({}^P\mathbf{G} - G_{00}\mathbf{P})^{-1} \mathbf{g}^\dagger = G_{00}^{-1},$$

which proves the equivalence of E_{as} and $f(\varepsilon)$, by comparison with Eqs.(15) and (16).

Finally, some notes on the lower bound property of Eq.(15) are due. While it is beneficial, that a strict lower bound can be obtained with an approximate eigenfunction of G , the value itself corresponds to a bound computed with the reference function. This means that no profit from solving the coefficient equation manifests in Eq.(15). It is appropriate to add here, that the lower bound feature of Eq.(15) applies only if the full space of excited functions is considered in the coefficient equation, Eq.(14). Once a truncation (CEPA0-type or other) is applied to space P , the equivalence of Eqs.(15) and (16) is dismissed.

It is also interesting to add, that comparing form

$$f(\varepsilon) = \varepsilon - \mathbf{h} ({}^P\mathbf{H} - \varepsilon\mathbf{P})^{-1} \mathbf{h}^\dagger$$

of the bracketing function with Eq.(15), one may wonder whether vectors $({}^P\mathbf{G} - G_{00}\mathbf{P})^{-1} \mathbf{g}^\dagger$ and $({}^P\mathbf{H} - \varepsilon\mathbf{P})^{-1} \mathbf{h}^\dagger$ are equivalent. This is not the case, it is only the scalar product of these vectors with \mathbf{h} which are equal.

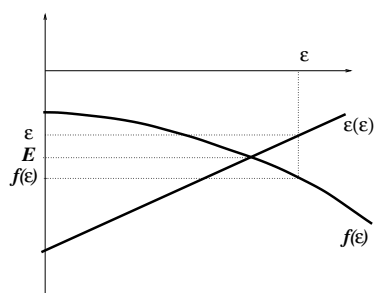


Fig. 1 Graphical illustration of the bracketing property of $f(\varepsilon)$ of Eq.(1).

4 Conclusion

The stationary condition of Löwdin's bracketing function leads to the eigenvalue equation of the resolvent. The bounding property of the energy formula is conditional, with a scalar playing a root controlling role. Based on the variational property and an Eckart-type inequality, Löwdin's bracketing function offers a way to refine a lower-bound systematically and improve the wavefunction simultaneously.

Applicability of the stationary condition is seriously hindered by the appearance of the resolvent. In practice, approximations are necessary for G , the nature of which are crucial from the point of view of theory (e.g. conservation of bounding property) as well as performance. It is possible to eliminate the resolvent by supposing a suitable form of the reference function, a technique applied e.g. in the inverse method for lower bounds. Further studies on the relation between this latter approach and the bracketing function may help to elucidate the conditions on scalar ε , necessary and sufficient for the bounding property of the outcome of the inverse method.

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References

1. P. Löwdin, Phys. Rev. A **139**, 357 (1965)
2. N.W. Bazley, Phys. Rev. **120**, 144 (1960)
3. N.W. Bazley, D.W. Fox, J. Math. Phys. **3**, 469 (1962)
4. P.S.C. Wang, The Journal of Chemical Physics **48**, 4131 (1968)
5. J. Čížek, E.R. Vrscaj, International Journal of Quantum Chemistry **28**, 665 (1985)
6. P.O. Löwdin, Int. J. Quantum Chem. **21**, 69 (1982)
7. P. Piecuch, S. Zarrabian, J. Paldus, J. Čížek, Phys. Rev. A **42**, 5155 (1990)
8. P.R. Surján, Á. Szabados, in *Fundamental World of Quantum Chemistry, A Tribute to the Memory of Per-Olov Löwdin*, vol. III, ed. by E.J. Brändas, E.S. Kryachko (Kluwer, Dordrecht, 2004), pp. 129–185
9. H. Meißner, J. Chem. Phys. **119**, 4126 (2003)
10. J. Čížek, J. Chem. Phys. **45**, 4256 (1966)

11. R. Ahlrichs, P. Scharf, *Adv. Chem. Phys.* **67**, 501 (1987)
12. J. MacDonald, *Phys. Rev.* **43**, 830 (1930)
13. A. Scrinzi, *Phys. Rev. A* **45**, 7787 (1992)
14. G. Temple, *Proc. R. Soc. Lond. A* **119**, 276 (1928)
15. M. Marmorino, *J. Math. Chem.* **31**, 197 (2002)
16. I. Mayer, *Simple Theorems, Proofs, and Derivations in Quantum Chemistry* (Kluwer, New York, 2003)
17. I. Mayer, *Theor. Chim. Acta* **104**, 163 (2000)
18. P.R. Nagy, P.R. Surján, Á. Szabados, *Theor. Chim. Acta* **131**, 1109 (2012)