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Variational Extensions of Lower Bounds to Expectation Values

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Generalized variational expressions are presented for calculating rigorous lower bounds to the true expectation value $\langle\Psi|F|\Psi\rangle$ of a positive semidefinite operator F. These extended formulas, which involve an additional variational function, always lead to an improvement over the results previously obtained. The improvement is illustrated numerically with an application to various properties of the helium-atom ground state.

I. INTRODUCTION

We have recently proposed a number of formulas[1-3] for calculating rigorous lower bounds to the true quantum-mechanical expectation value $\langle\Psi|F|\Psi\rangle$ of a positive semidefinite operator $F \geq 0$. These bounds are calculated in terms of some trial function ϕ which approximates the true wave function Ψ; in particular, one requires an estimate (strictly, a lower bound) for the overlap integral

$$S \equiv |\langle\phi|\Psi\rangle|$$

of these functions.[4]

It was recognized that the calculated lower bounds could be optimized with respect to any adjustable parameters in the approximation ϕ, so that one had a form of variational principle for each property under consideration. Here we wish to introduce an additional variational flexibility which allows one to always improve the previous results. The extended formulas therefore supersede our previous lower-bound formulas, and permit one to improve the calculated bounds by a more satisfactory variational procedure. In Sec. III, the new formulas are illustrated numerically with a simple standard application to various properties of the normal helium atom.

II. VARIATIONAL LOWER BOUNDS

To obtain the generalized variational form of the lower-bound formulas, we introduce an arbitrary variational function χ and consider the Gram determinant[1,5] G of the vectors $|\Psi\rangle$, $|\phi\rangle$, and $F|\chi\rangle$, where $|\Psi\rangle$ and $|\phi\rangle$ are normalized, and, as usual, all elements of G are assumed real. Noting that G must be non-negative we infer that

$$\langle\Psi|F^{\nu}|\chi\rangle \gtrless S\langle\chi|F^{\nu}|\phi\rangle \pm \delta F^{\nu}(1-S^2)^{1/2} \quad , \tag{1}$$

where δF^{ν} is defined by

$$(\delta F^{\nu})^2 \equiv \langle\chi|F^{2\nu}|\chi\rangle - \langle\chi|F^{\nu}|\phi\rangle^2 \quad , \tag{2}$$

and where F^{ν} denotes the νth power of the positive semidefinite Hermitian operator F. Applying Schwarz's inequality to the left-hand side of (1), we obtain the lower bound, valid for arbitrary ν and χ,

$$\langle\Psi|F|\Psi\rangle \geq \frac{[S\langle\chi|F^{\nu}|\phi\rangle - \delta F^{\nu}(1-S^2)^{1/2}]^2}{\langle\chi|F^{2\nu-1}|\chi\rangle} \tag{3}$$

so long as the expression in brackets is positive.

In formula (3), one can now freely vary both ϕ and χ, as well as ν, to maximize the lower bound. Of course, by taking $\chi = \phi$ we get back the result previously obtained,[1] but formula (3) will always improve this result for suitable χ. Note that as $S = |\langle\phi|\Psi\rangle| \to 1$, the lower bound again becomes exact in the limit $\chi \to \phi, \Psi(\nu = 1)$.

A similar extension is readily obtained for each of the three remaining lower-bound formulas which have been presented. These results may be readily inferred by choosing vectors $|\Psi\rangle$, $|\phi\rangle$, $F|\chi\rangle$, $H|\phi\rangle$ in Ref. 2, or by choosing $F^{1/2}|\Psi\rangle$, $F^{-1/2}|\phi\rangle$, $F^{\nu-1/2}|\chi\rangle$ in Ref. 3. The final results are found to be

$$\langle\Psi|F|\Psi\rangle \geq \frac{S^2}{\langle F^{-1}\rangle} + \frac{[S(\langle\chi|F^{\nu}|\phi\rangle\langle F^{-1}\rangle - \langle\chi|F^{\nu-1}|\phi\rangle) - \langle F^{-1}\rangle\delta F^{\nu}(1-S^2)^{1/2}]^2}{\langle F^{-1}\rangle(\langle\chi|F^{2\nu-1}|\chi\rangle\langle F^{-1}\rangle - \langle\chi|F^{\nu-1}|\phi\rangle^2)} \quad , \tag{4}$$

$$\langle\Psi|F|\Psi\rangle \geq \frac{[(S\alpha_{\nu} - \beta_{\nu}\gamma)/(\Delta H)^2]^2}{\langle\chi|F^{2\nu-1}|\chi\rangle} \quad , \tag{5}$$

TABLE I. Lower bounds to properties $\langle\Psi|F|\Psi\rangle$ of normal helium atom, calculated from formulas of the text in the screening approximation, and expressed as a percentage of the true value (Ref. 6). Entries in parentheses give previous results (Ref. 3), and the value of $\langle\phi|F|\phi\rangle$ for the energy optimized ϕ $(c=\frac{27}{16})$ is included for comparison.

Operator F	r_1^2	r_1	r_1^{-1}	r_1^{-2}	r_{12}^2	r_{12}	r_{12}^{-1}	r_{12}^{-2}
Formula (3)	83.9 (79.4)	92.9 (90.3)	82.1 (81.9)	39.1 (38.2)	71.6 (71.3)	84.3 (84.2)	90.5 (90.3)	59.1 (56.2)
Formula (4)	84.1 (79.7)	92.9 (90.5)	83.7 (82.6)	43.6 (43.3)	71.8 (71.7)	84.5 (84.5)	91.0 (91.0)	62.2 (62.2)
Formula (5)	85.1 (80.6)	92.9 (90.5)	85.7 (85.2)	46.1 (45.1)	74.8 (74.1)	86.2 (85.9)	93.3 (92.9)	74.1 (74.1)
Formula (6)	85.2 (80.7)	93.0 (90.6)	85.9 (85.2)	50.8 (50.6)	75.0 (74.5)	86.4 (86.2)	96.7 (96.7)	82.1 (82.1)
$\langle\phi\|F\|\phi\rangle$	88.3	95.7	100.0	94.6	83.7	91.1	111.5	129.6

TABLE II. Numerical values of parameters used in calculating bounds of Table I.

Operator F	r_1^2	r_1	r_1^{-1}	r_1^{-2}	r_{12}^2	r_{12}	r_{12}^{-1}	r_{12}^{-2}
Formula (3)								
b	1.606	1.629	1.699	1.956	1.569	1.507	1.860	2.116
c	1.265	1.381	1.767	1.728	1.459	1.467	1.786	1.745
ν	0.887	0.939	0.710	0.548	0.784	0.637	0.463	0.448
Formula (4)								
b	1.581	1.632	1.772	1.672	1.532	1.471	1.788	1.728
c	1.253	1.381	1.813	1.759	1.454	1.463	1.790	1.751
ν	0.843	0.948	0.177	0.454	0.707	0.373	0.087	0.351
Formula (5)								
b	1.630	1.636	1.565	1.861	1.599	1.560	1.861	2.025
c	1.264	1.386	1.677	1.646	1.445	1.468	1.945	2.002
ν	0.928	0.952	0.899	0.623	0.830	0.744	0.705	0.502
Formula (6)								
b	1.616	1.651	1.569	1.568	1.564	1.512	2.000	2.000
c	1.259	1.386	1.687	1.649	1.442	1.464	2.000	2.000
ν	0.901	1.007	0.767	0.593	0.759	0.481	1.000	0.500

$$\text{and}\quad \langle\Psi|F|\Psi\rangle \geq \frac{S^2}{\langle F^{-1}\rangle} + \frac{[\langle F^{-1}\rangle(S\alpha_\nu - \beta_\nu\gamma)/(\Delta H)^2 - S\langle\chi|F^{\nu-1}|\phi\rangle]^2}{\langle F^{-1}\rangle(\langle\chi|F^{2\nu-1}|\chi\rangle\langle F^{-1}\rangle - \langle\chi|F^{\nu-1}|\phi\rangle^2)} \quad , \tag{6}$$

where in each case the expression in brackets is supposed positive. Here we have introduced the abbreviations, for various operators B,

$$\langle B\rangle \equiv \langle\phi|B|\phi\rangle \quad , \tag{7a}$$

$$(\Delta B)^2 \equiv \langle B^2\rangle - \langle B\rangle^2 \quad , \tag{7b}$$

and in (5) and (6) the quantities α_ν, β_ν, γ are now defined by

$$\alpha_\nu \equiv \langle\chi|F^\nu|\phi\rangle(\Delta H)^2 + (\langle H\rangle - E_k)(\langle\chi|F^\nu|\phi\rangle\langle H\rangle - \langle\chi|F^\nu H|\phi\rangle) \quad , \tag{8a}$$

$$\beta_\nu^2 \equiv (\delta F^\nu)^2(\Delta H)^2 - (\langle\chi|F^\nu|\phi\rangle\langle H\rangle - \langle\chi|F^\nu H|\phi\rangle)^2 \quad , \tag{8b}$$

$$\gamma^2 \equiv (1-S^2)(\Delta H)^2 - S^2(\langle H\rangle - E_k)^2 \quad , \tag{8c}$$

where $H\Psi = E_k\Psi$ is the Schrödinger equation for the state in question.

Each of the more complicated formulas (4)–(6) requires certain additional information (more complicated matrix elements, knowledge of the eigenvalue E_k, etc.) for its computation, but each yields a better lower bound than the simpler formula (3). In particular, formula (6) must always give the best result for any particular choice of χ. Each formula also reverts back to the corresponding previous result[1–3] when we take the particular choice $\chi = \phi$. We note finally that in calculating δF of Eq. (2), as in calculating ΔF of Eq. (7), one should use the "symmetric-sum operator" described in Ref. 1 to strengthen the bound.

III. NUMERICAL ILLUSTRATION

To illustrate the numerical improvement obtained from formulas (3)–(6) over the previous results[3], we consider again the standard example of one- and two-electron properties $F = r_1^n, r_{12}^n, n = \pm 1, \pm 2$, of the normal helium atom. The lower bounds will be calculated entirely within the simple screening approximation, with

$$\phi \equiv (c^3/\pi)e^{-cr_1 - cr_2} \quad , \tag{9a}$$

$$\chi \equiv (b^3/\pi)e^{-br_1 - br_2} \quad . \tag{9b}$$

Table I exhibits lower bounds calculated from formulas (3)–(6) in the approximation (9), with the previous results[3] included in parentheses for comparison, and all values expressed as a percentage of the true value.[6] In all cases, the overlap S has been calculated using the "improved" method described in Refs. 1–3. Table II gives the corresponding optimum values of the variational parameters b, c, ν, as determined by Powell's method of conjugate directions.[7]

Table I shows that the numerical improvement is fairly small except for the operators r_1 and r_1^2, where the remaining error is reduced by about $\frac{1}{4}$. However, the relative advantage of formulas (3)–(6) will generally be more significant in cases where it is not practical to optimize ϕ or ν completely. Therefore, one should certainly consider this additional variational freedom in any numerical application.

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