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Inequalities Among $\langle r^n \rangle$ Based on Gram Determinants

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This paper considers determinantal inequalities based on 2×2 and 3×3 Gram determinants. The elements of these determinants are the expectation values $\langle r^m \rangle$, where r is the distance from the nucleus of a selected atom. The 2×2 Gram determinant involves $m = -1, 0, 1$, while the 3×3 Gram determinant involves $m = -1, 0, 1, 2, 3$. In the present work, for calculational purposes, it is assumed that the element $\langle r \rangle$ is unknown, while all the other elements of the 2×2 and 3×3 determinants are known. Lower bounds of $\langle r \rangle$ are then calculated from the 2×2 and 3×3 determinantal inequalities for the noble gas atoms He, Ne, Ar, Kr, and Xe. The calculated lower-bound values of $\langle r \rangle$ are compared with the quantum-mechanical values of $\langle r \rangle$ calculated by Boyd using the Roothaan-Hartree-Fock wave functions. It is found that the lower-bound value of $\langle r \rangle$ involving the 3×3 Gram determinant leads to a better agreement with the quantum-mechanical value of $\langle r \rangle$ than the lower-bound value of $\langle r \rangle$ involving the 2×2 Gram determinant. The implications of this finding are discussed.

INTRODUCTION

Determinantal inequalities[1] represent a special class of approximation procedures for obtaining bounds on a quantity. A general approach to the problem of bounding an unknown quantity, say ω, may be posed as follows.[1] Suppose ω appears in one element, or in several elements, of a determinant $\boldsymbol{D}$ of a given order, whose sign is known, and whose other elements are all known. In this case, $\boldsymbol{D}$ may be viewed as a polynomial in ω whose zeros lead to possible values of the unknown ω.

In what follows, attention is restricted to 2×2 and 3×3 Gram determinants.

Determinantal Inequalities Based on the Gram Determinant.

A Gram determinant is a determinant whose elements are definite integrals.[2] The simplest example is a 2×2 Gram determinant, represented by

$$\boldsymbol{D}_{2\times 2} = \begin{vmatrix} (f_1 f_1) & (f_1 f_2) \\ (f_2 f_1) & (f_2 f_2) \end{vmatrix}, \tag{1}$$

where

$$(f_i f_j) \equiv \int f_i f_j \, dr \,, \tag{2}$$

with integration limits over the domain of the functions $f_i(r)$ and $f_j(r)$.

The Gram determinant, given in Eq. (1), has the property that[1]

$$\boldsymbol{D}_{2\times 2} \geq 0 \,. \tag{3}$$

When the equality sign is used in Eq. (3), one speaks of the Gram inequality.[2] A lower bound to an element of a Gram determinant of a given order may be obtained from the relevant Gram inequality.

The present work considers 2×2 and 3×3 Gram determinants whose elements are expectation values of the powers of r, where r is the distance from the nucleus of a selected atom.

In the present work, it is assumed that the element $\langle r \rangle$ in the 2×2 and 3×3 Gram determinants is unknown. (The quantity $\langle r \rangle$ is, of course, known from quantum-mechanical calculations but the assumption is made for calculational purposes). The question is posed now: is the lower bound to $\langle r \rangle$ calculated from the determinantal inequality involving the 3×3 Gram determinant closer to the Roothaan-Hartree-Fock value[3] of $\langle r \rangle$ than the lower bound to $\langle r \rangle$ obtained from the inequality that involves the 2×2 Gram determinant? The answer appears to be yes for the noble gas atoms He, Ne, Ar, Kr, and Xe.

The finding is of interest since the 2×2 Gram determinant involves elements $\langle r^m \rangle$ with $m = -1, 0, 1$, while the 3×3 Gram determinant involves $\langle r^m \rangle$ with $m = -1, 0, 1, 2, 3$. This means, as we shall see, that an integral that contains r is »synthesized« in terms of integrals containing higher powers of r.

Calculations

In what follows, atomic units will be used. (The unit of length is the bohr, the unit of energy is the hartree).

A type of Gram determinants have been obtained by Gadre and Matcha,[4] who used the functions

$$f_n(r) = [4\pi r^{2n-1} \rho(r)]^{1/2} \qquad n = 1, 2, \ldots \,, \tag{4}$$

where $\rho(r)$ is the (position) electron density defined in the interval $0 \leq r \leq \infty$.

Introducing the (position) radial electron density $D(r)$ by

$$\rho(r) = \frac{1}{4\pi} r^{-2} D(r) \,, \tag{5}$$

one obtains for Eq. (1), with Eqs. (4) and (5),

$$\boldsymbol{D}_{2\times 2} = \begin{vmatrix} \int_0^\infty r^{-1} D(r)\, dr & \int_0^\infty D(r)\, dr \\ \int_0^\infty D(r)\, dr & \int_0^\infty r\, D(r)\, dr \end{vmatrix} . \tag{6}$$

Introducing the expectation values $\langle r^m \rangle$ by

$$\langle r^m \rangle = \int_0^\infty r^m D(r)\, dr \qquad m = -2, -1, 0, 1, 2, \ldots, \tag{7}$$

it follows that Eq. (6) becomes

$$\boldsymbol{D}_{2\times 2} = \begin{vmatrix} \langle r^{-1} \rangle & 1 \\ 1 & \langle r \rangle \end{vmatrix} . \tag{8}$$

Note that in Eq. (8) the normalization condition,

$$\langle r^0 \rangle = \int_0^\infty D(r)\, dr = 1 , \tag{9}$$

has been used.

The extension of the above steps for the derivation of a 3×3 Gram determinant is simple: the functions $f_1(r)$ and $f_2(r)$ in Eq. (4) are augmented by the function $f_3(r)$, and the elements of $\boldsymbol{D}_{3\times 3}$ are calculated. The result is

$$\boldsymbol{D}_{3\times 3} = \begin{vmatrix} \langle r^{-1} \rangle & 1 & \langle r \rangle \\ 1 & \langle r \rangle & \langle r^2 \rangle \\ \langle r \rangle & \langle r^2 \rangle & \langle r^3 \rangle \end{vmatrix} . \tag{10}$$

Putting the 2×2 and 3×3 Gram determinants in Eqs. (8) and (10) equal to zero, one may calculate the respective lower-bound values of $\langle r \rangle$. The calculations were performed for the noble gas atoms He, Ne, Ar, Kr, and Xe, using the $\langle r^{-1} \rangle$, $\langle r^2 \rangle$, and $\langle r^3 \rangle$ values of Boyd,[3] who obtained them with the Roothaan-Hartree-Fock wave functions of Clementi and Roetti.[5]

DISCUSSION

It is seen from the second column in Table I that the lower-bound values $\langle r \rangle_{\text{L.B.}}$, obtained from the 2×2 Gram determinantal inequality, decrease as one goes from He to Xe. A decreasing behavior broken at Ar, in column three of Table I, is exhibited by the $\langle r \rangle_{\text{R.H.F.}}$ values of Boyd.[3] Moving now to Table II, one sees from the second column of this table that the lower-bound values $\langle r \rangle_{\text{L.B.}}$, obtained from the 3×3 Gram determinantal inequality, decrease from He to Ne, and from Ar to Xe. The same behavior is exhibited in column three of Table II by the $\langle r \rangle_{\text{R.H.F.}}$ values of Boyd.[3]

TABLE I

Calculated lower bounds (L.B.) of $\langle r \rangle$, *quantum-mechanical (R.H.F.) values of* $\langle r \rangle$ *(in a.u.), and their ratios. The calculated values of* $\langle r \rangle$ *were obtained from the* 2×2 *determinant in Eq. (8) by putting it equal to zero. The quantum-mechanical values of* $\langle r \rangle$ *were taken from Ref. 3.*

Atom	$\langle r \rangle_{\text{L.B.}}$	$\langle r \rangle_{\text{R.H.F.}}$	$\langle r \rangle_{\text{L.B.}}/\langle r \rangle_{\text{R.H.F.}}$
He	0.593	0.927	0.640
Ne	0.321	0.789	0.407
Ar	0.258	0.893	0.289
Kr	0.197	0.729	0.270
Xe	0.170	0.723	0.235

TABLE II

Calculated lower bounds (L.B.) of $\langle r \rangle$, *quantum-mechanical (R.H.F.) values of* $\langle r \rangle$ *(in a.u.), and their ratios. The calculated values of* $\langle r \rangle$ *were obtained from the* 3×3 *determinant in Eq. (10) by putting it equal to zero. The quantum-mechanical values of* $\langle r \rangle$ *were taken from Ref. 3.*

Atom	$\langle r \rangle_{\text{L.B.}}$	$\langle r \rangle_{\text{R.H.F.}}$	$\langle r \rangle_{\text{L.B.}}/\langle r \rangle_{\text{R.H.F.}}$
He	0.887	0.927	0.957
Ne	0.715	0.789	0.906
Ar	0.782	0.893	0.876
Kr	0.602	0.729	0.826
Xe	0.578	0.723	0.799

A comparison of the $\langle r \rangle_{\text{L.B.}}$ $\langle r \rangle_{\text{R.H.F.}}$ ratios in the fourth column of Table I with those in the fourth column of Table II reveals that the $\langle r \rangle_{\text{L.B.}}$ values calculated from the 3×3 Gram determinantal inequality are closer to the $\langle r \rangle_{\text{R.H.F.}}$ values of Boyd[3] than the $\langle r \rangle_{\text{L.B.}}$ values calculated from the 2×2 Gram determinantal inequality.

The finding that the $\langle r \rangle_{\text{L.B.}}$ values from the 2×2 and 3×3 cases are not the same is not surprising. In the 2×2 case, $\langle r \rangle_{\text{L.B.}}$ is a function of $\langle r^{-1} \rangle$ *and* $\langle r^{0} \rangle$, while in the 3×3 case, $\langle r \rangle_{\text{L.B.}}$ is a function of $\langle r^{-1} \rangle$, $\langle r^{0} \rangle$, $\langle r^{2} \rangle$ and $\langle r^{3} \rangle$.

It does not seem promising to enter into speculation about the trends exhibited in the values of $\langle r \rangle_{\text{L.B.}}/\langle r \rangle_{\text{R.H.F.}}$ as one goes from He to Xe in column four of Tables I and II. About the only safe suggestion is that the trend is connected with the increase in the atomic number and, consequently, with the increase in the number of electrons distributed in an increasing number of shells as one moves from He to Xe.

It should be mentioned here, for the sake of completeness, that some general inequalities involving $\langle r^{m} \rangle$ have been established and applied to two-electron systems by Tsapline,[6] Blau *et al.*[7] and Gálvez.[8]

Finally, two recent papers (not dealing with two-electron systems) should also be mentioned. One of these papers is by Angulo and Dehesa,[9] who obtained inequalities for $\langle r^{m} \rangle \cdot \langle r^{m-2} \rangle$. The other paper is by Gálvez and Porras,[10] who obtained the inequalities $\langle r^{k-3} \rangle \geq (2Z/k) \langle r^{k-2} \rangle$, where Z is the atomic number and $k = 1, 2, 3$. Gálvez and Porras have also obtained more complicated inequalities that involve $\langle r^{k-3} \rangle$ (on

the left-hand side of the inequality), and $\langle r^{k-2} \rangle$, $\langle r^{k-1} \rangle$, $\langle r^k \rangle$ and k (on the right-hand side of the inequality).

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APPENDIX

To obtain the three roots,[11] one forms

$$G = \frac{b^2}{4} + \frac{a^2}{27} \tag{A1}$$

If G is larger than zero, there will be one real root and two conjugate imaginary roots; if G is equal to zero, there will be three real roots of which at least two are equal; if G is smaller than zero, there will be three real and unequal roots.

To proceed, one computes[11] ϕ from the expression

$$\cos \phi = \frac{-(b/2)}{\sqrt{-a^3/27}} \tag{A2}$$

In terms of ϕ and a one may write[11] now for the three roots:

$$2\sqrt{-\frac{a}{3}} \cos \frac{\phi}{3} \tag{A3}$$

$$2\sqrt{-\frac{a}{3}} \cos \left(\frac{\phi}{3} + 120^\circ \right) \tag{A4}$$

$$2\sqrt{-\frac{a}{3}} \cos \left(\frac{\phi}{3} + 240^\circ \right) \tag{A5}$$

As an example, He is considered. For this atom $a = -4.676645$ and $b = 3.48769$. With these numbers, Eq. (2) gives $\phi = 2.68147$, while Eqs. (A1), (A2), and (A3) give the roots 1.564, –2.468, and 0.904. The third root is listed in Table II for He. (The slight discrepancy is due to a different numerical procedure used to obtain the root listed in Table II.

SAŽETAK

Nejednakosti za $\langle r^n \rangle$ zasnovane na Gramovoj determinanti

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Razmotrene su nejednakosti za determinante drugog i trećeg reda čiji su elementi očekivane vrijednosti $\langle r^n \rangle$, gdje r predstavlja udaljenosti od atomske jezgre, a $n = -1, 0, 1$ za determinante drugog, te $n = -1, 0, 2, 3$, za one trećeg reda. Za oba reda determinanti dobivena je donja ocjena očekivane vrijednosti $\langle r \rangle$. Računi ove donje ocjene provedeni su za atome plemenitih plinova He, Ne, Ar, Kr i Xe, koristeći vrijednosti za $\langle R^n \rangle$, $n \neq 1$, što ih je dobio Boyd rabeći Clementijeve i Roettijeve analitičke valne funkcije kvalitete bliske Hartrre-Fockovoj.