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Gram Detereminantal Inequalities with Elements $<r^m>$ Obtained from Hylleraas Wave Functions for the ^{2}S States of the Three-Electron Systems Li, Be^+, B^{2+}, C^{3+}, N^{4+}, O^{5+}, F^{6+}, and Ne^{7+}

P. Csavinszky

Department of Physics and Astronomy, University of Maine, Orono, Maine 04469-5709, USA

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The present work considers 2 × 2, 3 × 3, 4 × 4, 5 × 5, and 6 × 6 Gram determinants whose elements are expecion values of r, where r is the distance from the nucleus of a three-electron system. The $<r^m>$ values considered are those of King and Dressesl, who evaluated the radial electronic density function in closed form for the ^{2}S states of three-electron systems that are described by Hylleraas-type wave functions. (The number of terms in the wave functions are the following: 233 for Li, 164 for Be^+, 201 for B^{2+}, and 213 for C^{3+}, N^{4+}, O^{5+}, F^{6+}, and Ne^{7+}). In the present work it is assumed, for purposes of illustration, that $<r^{-1}>$ is unknown. It is found that lower bounds to $<r^{-1}>$, calculated from the 2 × 2, 3 × 3, 4 × 4, 5 × 5, and 6 × 6 Gram determinantal inequalities converge to the literature values obtained in King and Dressel. (The literature values are those that have been obtained with wave functions more involved than those of King and Dressel).

INTRODUCTION

Determinantal inequalities[1] represent a special class of approximation procedures for obtaining bounds on a quantity, such as an expectation value $<r^m>$, where r is the distance from the nucleus of an atom or an ion.

A Gram determinant is a determinant whole 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

$$(f_i f_j) = \int f_i f_j \, \mathrm{d}r \tag{2}$$
$$i = 1, 2; \quad j = 1, 2 \quad ,$$

with integeration limits over the common 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. A lower bound (L.B.) to an element of a Gram determinant of given order may be obtained from the relevant Gram inequality.

The present work considers 2 × 2, 3 × 3, 4 × 4, 5 × 5, and 6 × 6 Gram determinants whose elements are expectation values of powers of r, where r is the distance from the nucleus of a selected three-electron system. To be specific, the present work uses the $<r^m>$ values of King and Dressel[3] for the ^2S states of the LiI isoelectronic series: Li, Be^+, B^{2+}, C^{3+}, N^{4+}, O^{5+}, F^{6+}, and Ne^{7+}. The $<r^m>$ values mentioned above were obtained in Ref. 3 by using Hylleraas[4] wave functions with a very large (> 100) number of variational parameters. (An approximation for the radial density function, needed for the evaluation of $<r^m>$ from Hylleraas-type wave functions is obtained by King and Dressel[3] in a closed form. For details of the quite involved calculations the reader is referred to Ref. 3).

In the present work, it is assumed that the element $<r^{-1}>$ in the 2 × 2, 3 × 3, 4 × 4, 5 × 5, and 6 × 6 Gram determinant is unknown. (The quantity $<r^{-1}>$ for the three-electron systems considered is, of course, known from the quantum-mechanical calculations of King and Dressel,[3] but the assumption that it is not known is made for the purposes of the present work).

The question is posed now: do the lower bounds to $<r^{-1}>$ calculated from the 2 × 2, 3 × 3, 4 × 4, 5 × 5 and 6 × 6 Gram inequalities converge to the value obtained in Ref. 3? The answer appears to be yes for the three-electron systems considered in this work.

This finding is of interest since $\boldsymbol{D}_{2\times 2}$, for instance, involves elements $<r^m>$ with $m = -1, 0, 1$; $\boldsymbol{D}_{3\times 3}$ has elements with $m = -1, 0, 1, 2, 3$; $\boldsymbol{D}_{4\times 4}$ involves elements with $m = -1, 0, 1, 2, 3, 4, 5$; $\boldsymbol{D}_{5\times 5}$ has elements with m = $-1, 0, 1, 2, 3, 4, 5, 6, 7$; while $\boldsymbol{D}_{6\times 6}$ has elements $<r^m>$ with $m = -1, 0, 1, 2,$

3, 4, 5, 6, 7, 8, 9. This means, that a quantity such as $<r^{-1}>$, is »synthetised« in terms of quantities 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,[5] who used the functions

$$f_n(r) = [4\pi r^{2n-1}\rho(r)]^{1/2} \qquad r = 1,\ 2,\ 3,\ \ldots \tag{4}$$

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

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).

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

Introducing the expectation values $<r^m>$ by

$$<r^m> = \int_0^\infty r^m D(r)\,\mathrm{d}r \quad m = -1, 0, 1, 2, \ldots \tag{7}$$

it follows that Eq. (6) can be written as

$$\boldsymbol{D}_{2\times 2} = \begin{vmatrix} <r^{-1}> & <r^0> \\ <r^0> & <r> \end{vmatrix} . \tag{8}$$

It is noted here that the King and Dressel[3] normalization condition, namely

$$<r^0> = \int_0^\infty D(r)\, \mathrm{d}r = 3 \ , \qquad (9)$$

has been used in Eq. (8).

The extension of the above steps for the derivation of the $\boldsymbol{D}_{3\times3}$, $\boldsymbol{D}_{4\times4}$, $\boldsymbol{D}_{5\times5}$, and $\boldsymbol{D}_{6\times6}$ Gram determinants is simple. The functions $f_1(r)$ and $f_2(r)$ in Eq. (4) are augmented by the functions $f_3(r)$, $f_4(r)$, $f_5(r)$ and $f_6(r)$.

The result for the $\boldsymbol{D}_{6\times6}$ Gram determinant is given by

$$\boldsymbol{D}_{6\times6} = \begin{vmatrix} <r^{-1}> & <r^0> & <r> & <r^2> & <r^3> & <r^4> \\ <r^0> & <r> & <r^2> & <r^3> & <r^4> & <r^5> \\ <r> & <r^2> & <r^3> & <r^4> & <r^5> & <r^6> \\ <r^2> & <r^3> & <r^4> & <r^5> & <r^6> & <r^7> \\ <r^3> & <r^4> & <r^5> & <r^6> & <r^7> & <r^8> \\ <r^4> & <r^5> & <r^6> & <r^7> & <r^8> & <r^9> \end{vmatrix}$$

The Gram determinants of lower order are obtained from Eq. (10) by striking out certain elements. For instance, $\boldsymbol{D}_{2\times2}$ is obtained by maintaining only the first two elements in the first and second rows. Similarly, $\boldsymbol{D}_{3\times3}$ is obtained by maintaining the first three elements in the first, second, and third row. The extension of this procedure to the determinants $\boldsymbol{D}_{4\times4}$ and $\boldsymbol{D}_{5\times5}$ is obvious.

The lower bound values for $<r^{-1}>$, obtained from the Gram determinantal inequalities $\boldsymbol{D}_{n\times n} = 0$ (n = 2, 3, 4, 5, 6), for the three-electron systems considered, are listed in Table I.

TABLE I

Calculated lower bounds, $<r^{-1}>_{\mathrm{L.B.}}$, for the three-electron systems listed in the first column of the table, using Gram determinants $\boldsymbol{D}_{n\times n}$ with n = 2, 3, 4, 5, 6

System	$<r^{-1}>_{\mathrm{L.B.}}$				
	$\boldsymbol{D}_{2\times2}$	$\boldsymbol{D}_{3\times3}$	$\boldsymbol{D}_{4\times4}$	$\boldsymbol{D}_{5\times5}$	$\boldsymbol{D}_{6\times6}$
Li	1.8037	3.2609	4.0008	4.2849	4.4602
Be^{+}	2.9019	4.9295	5.8822	6.3476	6.5705
B^{2+}	3.9424	6.5255	7.7036	8.2762	8.5073
C^{3+}	4.9647	8.1003	9.5099	10.2351	10.7209
N^{4+}	5.9788	9.6660	11.3082	12.1562	12.7263
O^{5+}	6.9885	11.2269	13.1027	14.0738	14.7267
F^{6+}	7.9956	12.7849	14.8951	15.9894	16.7258
Ne^{7+}	9.0011	14.3412	16.6860	17.9033	18.7248

DISCUSSION

It is seen from Table I that the lower bound values, $<r^{-1}>_{L.B.}$, increase for each three-electron system as one goes from the value obtained from $D_{2\times2} = 0$ to the value obtained from $D_{6\times6} = 0$. For the quantum mechanical values, $<r^{-1}>_{Q.M.}$, the rerader is referred to Tables IV–XI of Ref. 3.

The ratios $<r^{-1}>_{L.B.}/<r^{-1}>_{Q.M.}$ are tabulated in Table II. Inspection of Table II reveals that the ratios $<r^{-1}>_{L.B.}/<r^{-1}>_{Q.M.}$ increase for each three-electron system as one moves from the value obtained with $D_{2\times2} = 0$ from the value obtained with $D_{6\times6} = 0$.

From the fact that the $<r^{-1}>_{L.B.}/<r^{-1}>_{Q.M.}$ values, for each of the three-electron systems considered, are converging toward unity, one may conclude that Gram inequalities, of the type considered, represent a viable approximation approach for obtaining a lower bound on an element such as $<r^{-1}>$.

It should be mentioned here, for the sake of completeness, that Gram inequalities among $<r^m>$ involving a number of atoms have been investigated by Csavinszky.[6] In Ref. 6, the spherically-symmetrical atoms He, Ne, Ar, Kr, Xe; Li, Na, K, Rb; and Be, Mg, Cs, Sr have been considered. At this point, it is pointed out that these atoms have different numbers of electrons, while the present investigations focus on three-electron systems. It should also be mentioned here, for the sake of completeness, that inequalities of different types that involve $<r^m>$ have recently been estalished by a number of workers. One of these is by Angulo and Dehesa,[7] who obtained inequalities for $<r^m><r^{m-2}>$. Another paper is by Gálvez and Porras,[8] who obtained the inequalities $<r^{k-3}> \leq (2Z/k)\ <r^{k-2}>$, where Z is the atomic number and $k = 1, 2, 3$, (It is noted here that Gálvez and Porras[8] have also obtained more

TABLE II

Calculated ratios $<r^{-1}>_{L.B.}/<r^{-1}>_{Q.M.}$ (for $<r^{-1}>_{Q.M.}$ see Ref. 3), for the three-electron systems listed in the first column of the table, using Gram determinants $D_{n\times n}$ with $n = 2, 3, 4, 5, 6$

System	$<r^{-1}>_{L.B.}/<r^{-1}>_{Q.M.}$				
	$D_{2\times2}$	$D_{3\times3}$	$D_{4\times4}$	$D_{5\times5}$	$D_{6\times6}$
Li	0.3154	0.5703	0.6997	0.7494	0.7800
Be^{+}	0.3639	0.6182	0.7377	0.7961	0.8240
B^{2+}	0.3855	0.6382	0.7534	0.8094	0.8320
C^{3+}	0.3979	0.6493	0.7622	0.8204	0.8593
N^{4+}	0.4060	0.6564	0.7679	0.8255	0.8642
O^{5+}	0.4117	0.6613	0.7718	0.8290	0.8675
F^{6+}	0.4159	0.6650	0.7747	0.8316	0.8699
Ne^{7+}	0.4191	0.6677	0.7769	0.8336	0.8719

complicated inequalities that involve $<r^{k-3}>$ on the left-hand side of the inequality, and $<r^{k-2}>$, $<r^{k-1}>$, $<r^{k}>$, and k on the right-hand side of the inequality). Finally, a recent publication by Brownstein[9] involving inequalities for one-electron moments of r, is cited. None of these papers, however, have a direct bearing on the current investigations.

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SAŽETAK

Nejednadžbe preko Gramovih determinanti s elementima $<r^{m}>$ za Hylleraasove valne funkcije stanja ^{2}S trielektronskih sustava Li, Be^+, B^{2+}, C^{3+}, N^{4+}, O^{5+}, F^{6+}, i Ne^{7+}

P. Csavinszky

U radu se razmatraju Gramove determinante dimenzija 2 × 2, 3 × 3, 4 × 4, 5 × 5 i 6 × 6. Njihovi su elementi očekivane vrijednosti potencija od r, gdje je r udaljenost od jezgre u trielektronskom sustavu. Razmatrane su vrijednosti $<R^{m}>$ Kinga i Dressela koji su dobili analitičke izraze za radijalnu elektronsku gustoću stanja ^{2}S trielektronskih sustava opisanih valnim funkcijama Hylleraasova tipa. Broj članova u valnim funkcijama jest 233 za Li, 164 za Be^+, 201 za B^{2+}, i 213 za C^{3+}, N^{4+}, O^{5+}, F^{6+} i Ne^{7+}. U ovom se radu, ilustracije radi, pretpostavlja da je $<r^{-1}>$ nepoznat. Nađeno je da donje granice za $<r^{-1}>$, izračunane uz pomoć Gramovih determinanti (dimenzija 2 × 2, 3 × 3, 4 × 4, 5 × 5 i 6 × 6), konvergiraju literaturnim vrijednostima Kinga i Dressela.