

# Comment on “Rigorous Bounds for Thermodynamic Properties of Harmonic Solids”

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TABLE I. Ground-state energies at equilibrium separations.

Source	Ref.	$R_{\min}$ ( $a_0$ )	$-E_{\min}^a$	$-\Delta E_{\min}^a$	$\zeta_{\min}$
KH, $\psi_0$	1	1.55	0.9868972	0.1380712	0.35879
KH, $\psi_1$	1	1.48	1.1321059	0.2832799	0.42209
This work, $\psi_1$	...	1.55	0.9945540	0.1457277	0.36952
KH, $\psi_2$	1	1.47	1.1390731	0.2902471	0.42423
This work, $\psi_2$	...	1.53	1.0029703	0.1541439	0.37151
Kołos and Wolniewicz	9	1.40	1.1744746	0.1744746	...

<sup>a</sup> Energies in Hartree atomic units,  $e^2/a_0 = 27.2$  eV.

Our Eq. (2) agrees with KH, while Eq. (3) does not. In particular, we find

$$\langle s_B | 1/r_A | p_{zA} \rangle \neq \langle s_B | 1/r_B | p_{zA} \rangle \quad (4)$$

in contrast to KH. Thus, their conclusions based on  $\psi_1$  and  $\psi_2$  which give rise to the integrals in question need be re-examined; their results based on  $\psi_0$  alone are correct.

Differences between our recalculations<sup>6,7</sup> and those of KH corresponding to  $\psi_1$  and  $\psi_2$  are summarized in Table I and Fig. 1. We obtain larger equilibrium separations and higher minimum energies. Our binding energy<sup>8</sup> curves are all bounded from below by the exact one.<sup>9</sup> We find, in contrast to KH, that the addition of  $p_x$  and  $p_y$  terms affords substantial improvement in the energy near the equilibrium separation. Our variational parameter  $\zeta$  is quite different from theirs.

The main thrust of the KH article was to determine whether a simple Gaussian wavefunction would yield a potential curve with an error which is essentially constant over the whole range of internuclear separations. KH concluded that, especially for long-range interactions, Gaussians were not too promising. Our corrected binding energy curves<sup>6</sup> still don't fulfill the KH desideratum. Whether this goal is attainable by using Gaussian trial functions more sophisticated than that of Eq. (1) remains an open question.

Thanks are due J. O. Hirschfelder, W. A. Lester, Jr., and I. Shavitt for their helpful comments.

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<sup>1</sup> H. Kim and J. O. Hirschfelder, *J. Chem. Phys.* **47**, 1005 (1967).

<sup>2</sup> KH denote their three wavefunctions as  $\psi_0$ ,  $\psi_1$ , and  $\psi_2$ . They are obtained from Eq. (1) as follows:  $\psi_0$ :  $C_0^{(1)} = C_0^{(2)} = 0$ ;  $\psi_1$ :  $C_1^{(1)} = \alpha$ ,  $C_1^{(2)} = 0$ ;  $\psi_2$ :  $C_2^{(1)} = \beta$ ,  $C_2^{(2)} = \gamma$ .

<sup>3</sup> In both our and the KH calculations, the coordinate systems centered on the nuclei are both parallel and right handed.

<sup>4</sup> I. Shavitt, *Methods Computational Phys.* **2**, 1 (1963).

<sup>5</sup> In Eqs. (2) and (3),

$$F(x) = \left(\frac{1}{2}\right) (\pi/x)^{1/2} \operatorname{erf}(x^{1/2}) \\ = \int_0^1 \exp(-xu^2) du, \quad (x > 0).$$

<sup>6</sup> S. L. Brenner, B. A. thesis, Harpur College, State University of New York at Binghamton, 1969, gives detailed results.

<sup>7</sup> The following programs, obtained from the Quantum Chemistry Program Exchange, Indiana University, were used in our calculations: F. Prosser, GIVENS, Program 62.1; H. H. Michels and P. Elliott, NESBET, Program 93, and CEIG, Program 97; J. P. Chandler, SIMPLEX, Program 67.

<sup>8</sup> Following KH, the binding energy is defined as  $\Delta E_R = E_R - E_\infty$ , where  $E_\infty = 2(-4/3\pi) = -0.848826$  a.u., and  $\zeta_\infty = 8/9\pi = 0.282942$ .

<sup>9</sup> Compare with the nearly exact results of W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **43**, 2429 (1965).

## Comment on "Rigorous Bounds for Thermodynamic Properties of Harmonic Solids"

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In a recent paper<sup>1</sup> Wheeler and Gordon used Chebyshev inequalities and the moments of the lattice frequency spectrum,  $G(x)$  in their notation, to derive inequalities on various quantities, including the integrated frequency spectrum,

$$\int_0^\infty dx G(x).$$

Their bounds, at least on this latter integral, may be improved by employing other information about  $G(x)$ , namely, that it is bounded. Their figure shows  $G(x)$  to have a bound of about 2.06. Using this bound gives the improved bounds on

$$\int_0^\infty dx G(x)$$

shown in Fig. 1. As in Ref. 1, the marked points are the calculated points, and the lines have been interpolated. Using the more conservative upper bound on  $G(x)$  of 3 gives bounds on the integral rather closer to the inner set than to the outer. The method follows the analysis of Mallows,<sup>2</sup> and briefly, is this. If the density function, in this case  $G(x)$ , is known to have a bound of  $L$ , say, then extremal distributions may be formed of sums of rectangles— $f_i(x) = L$  for  $a_i < x < b_i$ , = 0 otherwise—

rather than  $\delta$  functions. The fundamental integral of the theory is (see, for example, Shohat and Tamarkin<sup>3</sup>)

$$I(z) = \int_{-\infty}^{\infty} \frac{dxG(x)}{(z-x)} \sim \frac{\mu_0}{z} + \frac{\mu_1}{z^2} + \dots,$$

the  $\mu_i$  being moments of  $G$ . Substituting the "sum of rectangles," trial distribution for  $G$  gives

$$\exp[L^{-1}I(z)] = \prod_i [(z-a_i)/(z-b_i)].$$

Thus, the  $a_i$  and  $b_i$  are the roots of numerator and denominator polynomials, respectively, obtained as successive approximations to the continued fraction representation<sup>4</sup> of the expansion of

$$\exp[L^{-1}(\mu_0/z + \mu_1/z^2 + \dots)]$$

in powers of  $1/z$ .

The computing was done on AECL's CDC-6600 computer, using double-precision arithmetic to derive the recurrence-relation coefficients for the continued fractions (after the method of Wall,<sup>4</sup> Chap. XI). The set of recurrence relations was written as an  $n \times n$  tridiagonal matrix (as in Ref. 5, for instance), whose eigenvalues are the roots of the  $n$ th-order polynomial. The matrix was diagonalized using single-precision arithmetic; improved values of the eigenvalues were then found by evaluating the polynomial and its derivative at each eigenvalue (using the recurrence relation in double precision) and extrapolating to zero.

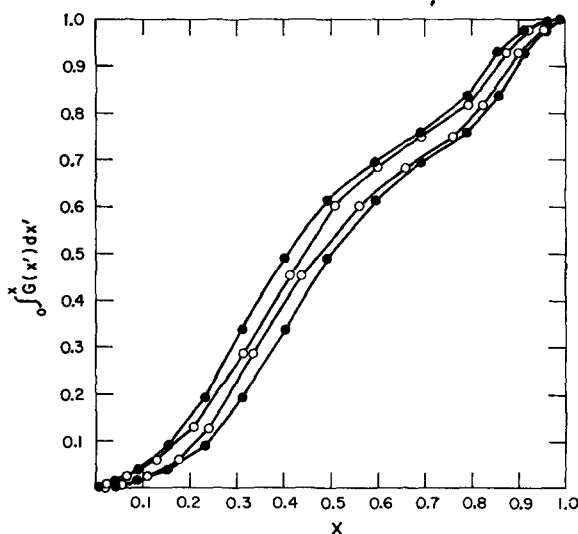


FIG. 1. Upper and lower bounds to the cumulative distribution

$$\int_0^{\infty} dx'G(x')$$

as in Fig. 1 of Ref. 1. The points are calculated, and the straight lines interpolated. Solid circles correspond to unbounded density (as in Ref. 1), open circles to bounded density with  $G(x) \leq 2.06$ .

In the repetition of the calculation of Ref. 1, the Gaussian-integration points and weights of Table II were reproduced to 10 significant figures. In both calculations shown in Fig. 1 the original moments were reproduced to  $2 \times 10^{-14}$  or better.

To improve the precision of the numerical exponentiation of the power series, the identity

$$\begin{aligned} \exp\left(L^{-1}\sum_i \frac{\mu_i}{z^{i+1}}\right) &= \exp\left(L^{-1}\sum_i \frac{\mu_i - C\zeta^{i+1}/i+1}{z^{i+1}} + \frac{C\zeta^{i+1}}{(i+1)z^{i+1}}\right) \\ &= \left(1 - \frac{\zeta}{z}\right)^{-CL^{-1}} \exp\left(L^{-1}\sum_i \frac{\mu_i - C\zeta^{i+1}/i+1}{z^{i+1}}\right) \end{aligned}$$

was used, with  $\zeta$  and  $C$  chosen to make the last two values of  $\mu_i - C\zeta^{i+1}/i+1$  equal to zero.

The purpose of this note is to point out that these improved bounds can be calculated, and that they are substantial improvements over the bounds obtained by the classical Chebyshev inequalities. If the actual values of the bounds were the primary interest, one would make two improvements. First, the maximum value of the density, in this case the value of  $G(x)$  at the cusp, would be calculated, rather than taken from a figure. Since in this case the maximum is a cusp, this is not so important, for the area of the upper part of a cusp is small. Alternatively, some part of the cusp could be subtracted and dealt with separately as Wheeler and Gordon did with the  $x=0$  end of the spectrum. The second improvement would be to adjust the recurrence-relation coefficients at each stage of the calculation by using a least-squares fitting routine to fit the moments better. It is expected that this also would cause little change in the bounds. A proper error analysis of the Chebyshev inequalities calculations has not, to the author's knowledge, been done. The author's observations, based on a few hundred such calculations, is that small changes in the moments make small changes in the bounds—the large shifts in the Gaussian integration points are compensated by the large shifts in the weights. However, once the errors exceed some critical size, they rapidly become huge. This trouble occurs in the calculation of the recurrence relation coefficients, where one is subtracting nearly equal large numbers.

It may be mentioned in passing that inequalities such as these are useful also in the solution of integral equations in which it is easy to calculate moments and harder to find solutions.

<sup>1</sup> J. C. Wheeler and R. G. Gordon, *J. Chem. Phys.* **51**, 5566 (1969).

<sup>2</sup> C. L. Mallows, *J. Roy. Stat. Soc.* **B18**, 139 (1956).

<sup>3</sup> J. A. Shohat and J. D. Tamarkin, *The Problem of Moments* (American Mathematical Society, New York, 1943), Mathematical Surveys No. 1.

<sup>4</sup> H. S. Wall, *Analytic Theory of Continued Fractions* (Van Nostrand, New York, 1948).

<sup>5</sup> G. H. Golub and J. H. Welsch, *Math. Computation* **23**, 221 (1969).