

## Spin-polarized quantum systems: Internal energies through a lower-bound formula and the quantum theorem of corresponding states

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An extension of de Boer's quantum theorem of corresponding states, which yields a relation between the minimum number of atoms required in a cluster so that it behaves like the bulk system  $N_{\min}$  and de Boer's quantum parameter  $\Lambda^*$ , is realizable when Hall-Post-Stenschke lower-bound energies are matched with the experimental internal energies of the condensed phase of spin-polarized quantum systems and rare-gas atoms. Through it is found evidence that both forms of spin-polarized deuterium have bound ground states, that spin-polarized helium has an internal energy of  $-2.1$  K per atom, and that  $N_{\min}$  ranges from 6 to 19.

The astounding properties predicted to exist in spin-polarized quantum systems of atomic hydrogen, its isotopes, and  ${}^3\text{He}$  (labeled  $\text{H}\uparrow$ ,  $\text{D}\uparrow$ ,  $\text{T}\uparrow$ , and  ${}^3\text{He}\uparrow$ , respectively) have captured the attention of a large group of physicists.<sup>1,2</sup> Thus the study of these systems has burgeoned into a highly active area of research which has brought together in a common endeavor participants normally separated from each other in disparate disciplines. Happily too, the intense interest has been sustained by rapid developments in the experimental stabilization of  $\text{H}\uparrow$ .<sup>3</sup> Theoretically, while the properties of  $\text{H}\uparrow$  are reasonably well delineated, those of  $\text{D}\uparrow$  and  ${}^3\text{He}\uparrow$  fermionic systems, as opposed to the bosonic  $\text{H}\uparrow$ , are much less certain.<sup>2,4</sup> For example, the macroscopic states of the two forms of spin-polarized deuterium,  $\text{D}\uparrow_1$  and  $\text{D}\uparrow_2$  (corresponding to the two possible nuclear-spin configurations), and the internal energy per atom of  ${}^3\text{He}\uparrow$ , are undetermined.

Hess reports seeing clusters of  $\text{D}\uparrow$  at 1.5 K and in 50-kG magnetic fields,<sup>5</sup> but variational calculations<sup>4,6,7</sup> and empirical extensions of the quantum theorem of corresponding states (QTCS) of de Boer<sup>8,9</sup> yield differing "opinions," an illustration of how close  $\text{D}\uparrow$  is to the critical boundary between gas and liquid at low temperatures. Miller and Nosanow,<sup>4</sup> who used the Bogoliubov-Born-Green-Kirkwood-Yvon-Kirkwood-superposition-approximation (BBGKY-KSA) procedure to evaluate radial distribution functions corresponding to Jastrow functions and the Wu-Feenberg antisymmetrization expansion, found that  $\text{D}\uparrow_1$  and  $\text{D}\uparrow_2$  have bound states, but because the energies derived (0.13 K/atom for  $\text{D}\uparrow_1$  and 0.23 K/atom for  $\text{D}\uparrow_2$ ) were very small, they were justifiably hesitant to make that claim. The general difficulty of treating fermionic  $N$ -body systems<sup>10</sup> extends also to  ${}^3\text{He}\uparrow$ , where the largest energy obtained is  $-1.75$  K/atom as reported in Ref. 11, but the authors are chary of having ob-

tained a convergent result.

In this climate of doubt, one is gratified to locate circumstantial, but compelling evidence which suggests that both  $\text{D}\uparrow_1$  and  $\text{D}\uparrow_2$  have bound ground states (energies 0.1 and 0.28 K/atom, respectively) and that  ${}^3\text{He}\uparrow$  has an energy of  $-2.1$  K/atom. Simultaneously the analysis reported herein yields another important number which holds much interest for researchers in the area of nucleation theory, nozzle beam work, and colloid chemistry, namely, the minimum number of atoms in a cluster which makes it behave like the bulk system.<sup>12</sup> For "classical" substances this number is 19.

This work began as an attempt to update and improve a paper of Etters.<sup>13</sup> In it, he determined the absolute Hall-Post-Stenschke lower-bound energy<sup>14</sup> for small clusters of  $\text{H}\uparrow$  and  $\text{D}\uparrow$ , then concluded that, since at least nine atoms of  $\text{H}\uparrow$  and five of  $\text{D}\uparrow$  were needed for binding, a plausible argument based on a direct comparison of these numbers with that required to yield the experimentally determined energy of  ${}^4\text{He}$ ,  $N_{\min}({}^4\text{He}) \simeq 8$ , implies that  $\text{H}\uparrow$  is undoubtedly gaseous at 0 K. He felt that the existence of liquid  $\text{D}\uparrow$  is an open question.

Etters's arguments include the following assumptions. First, the diatomic potential, required in the lower-bound formula [ $E_N(m) \geq \frac{1}{2}N(N-1) \times E_2(Nm/2)$ ], where  $E_N(m)$  is the absolute lower-bound energy for a cluster of  $N$  identical atoms each of mass  $m$  and  $E_2(Nm/2)$  is the exact energy for a diatomic pair identical in every way to the atoms in the cluster but with a mass  $Nm/2$ ] has now been superseded by more accurate phenomenological representatives, not all of which have the Morse form.<sup>4,15,16</sup> Second, account must be taken of the requirements of symmetry in the two-body problem. This implies that the lowest  $P$ -wave state must be used in place of the  $S$ -wave ground state for the description of fermions.<sup>17</sup> Third, it should not be

$^4\text{He}$  alone which serves as the final arbiter of the macroscopic properties of the other light-element systems.

The first two deficiencies are rectified by using Morse fits to the potential of Kolos and Wolniewicz<sup>16</sup> for the hydrogen isotopes and to that of Aziz *et al.*<sup>15</sup> for the He isotopes. The prescription selected for this procedure is that the maximum depth ( $\epsilon$ ), its location ( $r_{\min}$ ), and the zero-potential point ( $\sigma$ ) of the accurate potential are exactly yielded by the Morse potential,

$$V_M(r) = \epsilon \{ \exp[-2\alpha(r - r_{\min})] - 2 \exp[-\alpha(r - r_{\min})] \} \quad (1)$$

This decision to stay with the Morse potential as the common denominator for the systems studied lies not only in its computational simplicity— $S$  states are exactly evaluated while an excellent perturbative approximation exists for the  $P$  states<sup>18</sup>—but also in its accurate description of the bowl region, the region of greatest importance in the binding-energy calculations. The role played by other well known systems in explicating the macroscopic properties of  $D\uparrow$  and  $^3\text{He}\uparrow$  [well known in the sense that their true internal energies are accurately pegged, as in  $^3\text{He-B}$ — $^3\text{He}$  atoms treated as bosons—and  $T\uparrow$  (Refs. 19 and 20)] is not easily clarified. However, there is a suggestion when one develops the  $E_N/N$  vs  $N$  curves for  $^3\text{He-B}$ ,  $T\uparrow$ ,  $^4\text{He}$ ,  $D-B$ —deuterium atoms treated as bosons—and  $H\uparrow$ , and evaluates  $N_{\min}$  for  $^3\text{He-B}$ ,  $T\uparrow$ , and  $^4\text{He}$  (where the energy for  $^3\text{He-B}$  is given in Ref. 19, that for  $T\uparrow$  is on Table III of Ref. 20 and that for  $^4\text{He}$  is quoted in Ref. 21). Then if one checks these values off on the energy versus  $N$  plots (see Fig. 1), one can discern the makings of a universal curve passing through the three points. In Ref. 9, de Boer had empirically shown a curve for  $U_0^*$ , the internal energy in reduced energy units, versus  $\Lambda^*$  [where  $\Lambda^* = 2\pi\eta^{1/2} = (\hbar^2/m\epsilon\sigma^2)^{1/2}$  is the quantum parameter], on and astride which sit the points extracted from the internal energies of a number of elements in their condensed phases. It becomes conceivable that  $N_{\min}$  and  $\Lambda^*$  can also be closely correlated. A plot of these two quantities for  $^3\text{He-B}$ ,  $T\uparrow$ ,  $^4\text{He}$ , and the heavier rare-gas atoms [for these the same procedure as for the light elements is followed and the parameters quoted in de Boer's work are used (see Table I)], is shown in Fig. 2. Indeed, there materializes a universal curve for these bosons from which one can reliably extract the value  $N_{\min}(D-B) = 6.4$ . Returning then to Fig. 1 and checking this number off on the  $D-B$  curve indicates an internal energy of 0.65 K/atom for  $D-B$ . More interestingly for the matter at hand, one finds that a smooth curve passes through these four  $N_{\min}$  points, intersecting the  $O$  line at  $N = N_{\text{crit}}^B = 6.3$ . This latter curve is nowhere near the  $H\uparrow$  line (the arrow in Fig. 1 indicates where the

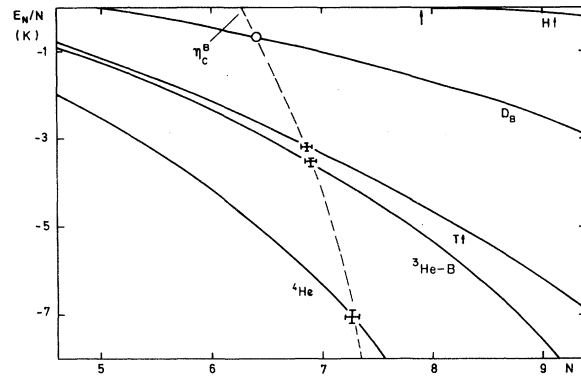


FIG. 1. Plot of  $E_N/N$  against  $N$  for a number of bosonic systems.  $N_{\min}$  is obtained by locating the positions of the “true” energies of the elements on the appropriate Hall-Post-Stenschke curves. The dashed line is the boson universal curve.

$H\uparrow$  curve meets the  $O$  axis). Accordingly,  $H\uparrow$  does not possess an  $N_{\min}$  value for negative energies and cannot have a bound ground state, in line with expectation. Also  $N_{\text{crit}}^B = 6.3$  implies a critical value for  $\eta$  in bosons, viz.,  $\eta_c^B = 0.46$  in embarrassingly good agreement with the Miller-Nosanow and Bruch values.<sup>4,22</sup>

Proceeding now to the fermionic systems, one expects to find a universal curve here for  $N_{\min}$  vs  $\Lambda^*$  as well in both the “totally” fermionic ( $D\uparrow_1$ ,  $^3\text{He}\uparrow$ , etc.)

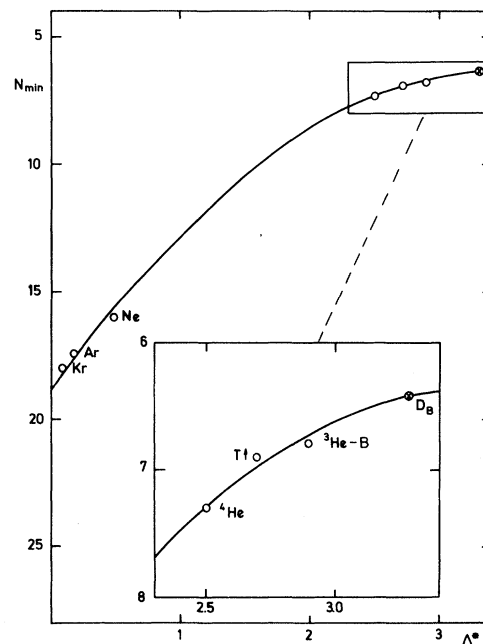


FIG. 2. Plot of  $N_{\min}$  against the de Boer parameter  $\Lambda^*$  for rare-gas and other bosonic atoms.

TABLE I. Table of potential parameters,  $N_{\min}$  (the minimum number of atoms in a cluster to yield macroscopic energies), and  $U_0^*$  (the reduced internal energy in the condensed phase) for various elements. (The values of  $U_0^*$  in the last four lines of this table were obtained through methods described in this paper.)

System	$\epsilon$ (K)	$r_{\min}$ (Å)	$\sigma$ (Å)	$\alpha$ (Å)	$\eta$	$\Lambda^*$	$N_{\min}$	$U_0^*$
Kr	201.9	4.004	3.569	1.59	2.251-4	0.094	17.9	8.1 <sup>a</sup>
Ar	142.1	3.760	3.351	1.69	7.616-4	0.173	17.4	7.7 <sup>a</sup>
Ne	42.0	3.372	2.764	1.89	7.498-3	0.542	16.0	6.4 <sup>a</sup>
<sup>4</sup> He	10.85	2.968	2.643	2.02	0.1599	2.50	7.3	0.66 <sup>b</sup>
T $\uparrow$	6.462	4.153	3.69	1.46	0.183	2.69	6.9	0.50 <sup>c</sup>
<sup>3</sup> He-B	10.85	2.968	2.643	2.02	0.2122	2.89	6.8	0.33 <sup>d</sup>
<sup>3</sup> He	10.85	2.968	2.643	2.02	0.2122	2.89	· · ·	0.23 <sup>d</sup>
D-B	6.462	4.153	3.69	1.46	0.274	3.28	6.4	0.10
<sup>3</sup> He $\uparrow$	10.85	2.968	2.643	2.02	0.2122	2.89	7.9	0.19
D $\uparrow_1$	6.462	4.153	3.69	1.46	0.274	3.28	7.6	0.016
D $\uparrow_2$	6.462	4.153	3.69	1.46	0.274	3.28	· · ·	0.043

<sup>a</sup>Quoted from Ref. 9.

<sup>b</sup>Computed from the experimental internal energy per atom quoted in Ref. 21.

<sup>c</sup>Computed from the variational internal energy per atom listed in Table III of Ref. 20.

<sup>d</sup>Computed from the calculated value of Ref. 19.

and “mixed” fermionic (D $\uparrow_2$ , <sup>3</sup>He, etc.) systems but one is thwarted since there are no  $U_0^*$  values available to fix  $N_{\min}$ . However, the recent work of Lee *et al.*<sup>19</sup> on <sup>3</sup>He and <sup>3</sup>He-B does suggest an “experimentally determined” energy of <sup>3</sup>He $\uparrow$ . By appropriate spin weighting,<sup>23</sup> one sees that to a good approximation

$$E_{3\text{He}} = \frac{3}{4}E_{3\text{He}\uparrow} + \frac{1}{4}E_{3\text{He-B}} \quad (2)$$

Thus, since  $E_{3\text{He}} = -2.47$  K/atom and  $E_{3\text{He-B}} = -3.54$  K/atom,  $E_{3\text{He}\uparrow} = 2.1$  K/atom. This value is probably closer to the “true” energy of <sup>3</sup>He $\uparrow$  than the variationally determined  $-1.75$  K/atom calculated by Lhuillier and Levesque<sup>11</sup> since Eq. (2) is a reliable relation and the energy values used in it are very accurate. In fact, Clark *et al.* have also suggested a value around  $-2.0$  K/atom.<sup>6</sup> Going to Fig. 3, where the  $E_N/N$  vs  $N$  curves are plotted for fermions and with  $-2.1$  K/atom as the fix for the totally fermionic curve, one can draw a line with the same slope as for bosons through it. This curve intersects D $\uparrow_1$  at  $N_{\min} = 7.6$  suggesting an energy of 0.10 K/atom for this system. One can also use a similar spin-weighting estimate to find the energy for D $\uparrow_2$  since one already has the energies for D-B and D $\uparrow_1$ . In fact

$$E_{D\uparrow_2} = \frac{2}{3}E_{D\uparrow_1} + \frac{1}{3}E_{D-B} \quad (3)$$

yields an internal energy of  $-0.28$  K/atom for D $\uparrow_2$ .

The universal curve for the totally fermionic species crosses the  $O$  axis with  $N_{\text{crit}}$  just a shade under 7.6, thus giving  $\eta_c^{FT} = 0.29$ . These values for the totally fermionic systems are again in excellent agreement with the values of Miller and Nosanow.<sup>4</sup> For the mixed fermions, the projected universal curve yields  $\eta_c^{FT} = 0.27$ .

The numerical predictions of this analysis should not depend sensitively on any of the assumptions made. D-B is definitely bound and Eq. (3) implies that D $\uparrow_2$  is bound irrespective of whether D $\uparrow_1$  is or is

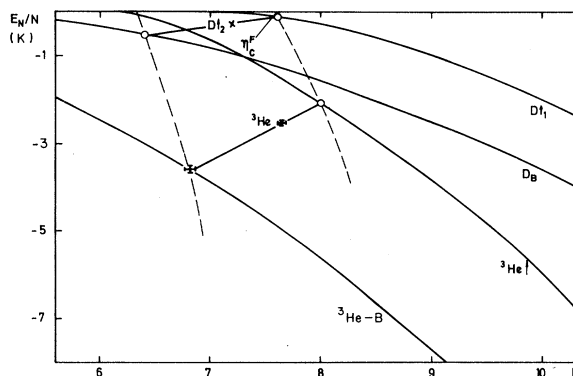


FIG. 3. Plot of  $E_N/N$  against  $N$  for a number of bosonic and fermionic systems. The dashed lines are the universal curves mentioned in the text.

not itself bound. As to the latter point, it would take a large shift of the totally fermionic curve to make  $D\uparrow_1$  unbound. This is possible but not likely. Another reason why one expects no dramatic change in the totally fermionic curve is that the boson and two fermion curves must almost coalesce as  $N_{\min}$  grows and the systems become more classical. In fact, there is a limiting value for  $N_{\min}$ . From Fig. 2 this is 19, which is to be contrasted with a value between 6 and 8 for a quantum-mechanical system. These numbers compare favorably with those obtained by Sinanoglu.<sup>12</sup>

To conclude there exists an extension of de Boer's QTCS which embodies a direct relationship between the parameter  $\Lambda^*$  (and thus also  $\eta$ ) and  $N_{\min}$  (the quantity obtained from matching the Hall-Post-Stenschke lower-bound energy to that experimentally determined) for rare gases and spin-polarized quantum systems. This connection implies bound ground

states for  $D\uparrow_1$  and  $D\uparrow_2$  and predicts an acceptable internal energy for  $^3\text{He}\downarrow$ . It would be interesting to repeat the analysis of this paper for two-dimensional systems. Work in this direction is in progress.

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<sup>1</sup>J. Phys. (Paris) **41** (1980).

<sup>2</sup>L. H. Nosanow, J. Phys. (Paris) **41**, C7-1 (1980).

<sup>3</sup>I. F. Silvera and J. T. M. Walraven, J. Appl. Phys. **52**, 2304 (1981).

<sup>4</sup>M. D. Miller and L. H. Nosanow, Phys. Rev. B **15**, 4376 (1977).

<sup>5</sup>R. Hess, Ph.D. thesis (University of Stuttgart, W. Germany, 1971) (unpublished).

<sup>6</sup>J. W. Clark, E. Krotscheck, and R. M. Panoff, J. Phys. (Paris) **41**, C7-197 (1980).

<sup>7</sup>J. V. Dugan, Jr., and R. D. Ethers, J. Chem. Phys. **59**, 6171 (1973); R. D. Ethers, J. V. Dugan, Jr., and R. W. Palmer, *ibid.* **62**, 313 (1975).

<sup>8</sup>C. Hecht, Phys. Rev. B **23**, 3547 (1981).

<sup>9</sup>J. de Boer, Physica (Utrecht) **14**, 139 (1948).

<sup>10</sup>G. A. Baker, Jr., in *Recent Progress in Many-Body Theories*, Lecture Notes in Physics, edited by J. Zabolitsky, M. de Llano, M. Fortes, and J. W. Clark (Springer-Verlag, Berlin, 1981), Vol. 142, p. 164.

<sup>11</sup>C. Lhuillier and D. Levesque, Phys. Rev. B **23**, 2203 (1981).

<sup>12</sup>O. Sinanoglu, Chem. Phys. Lett. **81**, 188 (1981).

<sup>13</sup>R. D. Ethers, Phys. Lett. **42A**, 439 (1973).

<sup>14</sup>R. L. Hall and H. R. Post, Proc. Phys. Soc. London **90**, 381 (1967); H. Stenschke, J. Chem. Phys. **53**, 466 (1970).

<sup>15</sup>R. A. Aziz, V. P. S. Nain, J. S. Carley, W. J. Taylor, and G. T. McConvile, J. Chem. Phys. **70**, 4330 (1979).

<sup>16</sup>W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965); Chem. Phys. Lett. **24**, 457 (1974).

<sup>17</sup>F. Calogero and C. Marchioro, J. Math. Phys. **10**, 562 (1969).

<sup>18</sup>S. Flugge, *Practical Quantum Mechanics* (Springer-Verlag, Berlin, 1971), Vol. 1, p. 186.

<sup>19</sup>M. A. Lee, K. E. Schmidt, M. H. Kalos, and G. V. Chester, Phys. Rev. Lett. **46**, 728 (1981).

<sup>20</sup>M. D. Miller, Phys. Rev. B **18**, 4730 (1978).

<sup>21</sup>M. H. Kalos, M. A. Lee, P. A. Whitlock, and G. V. Chester, Phys. Rev. B **24**, 115 (1981).

<sup>22</sup>L. W. Bruch, Phys. Rev. B **13**, 2873 (1976).

<sup>23</sup>T. K. Lim and S. Y. Larsen, J. Chem. Phys. **74**, 4997 (1981).