

# Is spin-aligned hydrogen a Bose gas?<sup>a)</sup>

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(Received 13 March 1979; accepted 5 September 1979)

In the last few years there has been a renewed interest in the possibility of preparing spin-aligned hydrogen atoms under conditions of low enough temperature ( $\sim 10$  mK), high enough magnetic field ( $\sim 100$  KG), and high enough density ( $\sim 10^{19}$  molecules/cc) that it will undergo a Bose condensation to a quantum Bose gas.<sup>1-5</sup> The assumption of Bose statistics appears at present to be a simple consequence of the fact that each H atom is composed of a pair of fermions. Such an argument is, of course, true for the statistics of say <sup>4</sup>He with a nucleus composed of an even number of fermions, since permutation of He atoms involves the exchange of such nuclei which are bosons. But is such an argument appropriate when the exchange involves two very different particles, viz an electron and a proton, which have different interactions with the other H atoms? In fact, it is the permutation symmetry of all the electrons separately as well as all the protons separately to which the Pauli Principle applies. The statement at this level that H atoms would be Bose particles would be equivalent to distinguishing a particular electron-proton pair as "going together" rather than acknowledging the indistinguishability of electrons with respect to each proton and *visa versa*. Of course, such an indistinguishability would not be of practical consequence if there were no feasible means whereby, e.g., electrons could exchange.<sup>6</sup> But, in the interacting dense gas of H atoms there will be a significant exchange interaction between the electrons, which, from a many-body point of view leads to a renormalized, density-dependent exchange interaction.<sup>3</sup>

It thus appears that we must be more careful in determining the statistics of a collection of H atoms. It is clear, from the quantum-fluid properties of <sup>4</sup>He and of <sup>3</sup>He, that their respective properties as bosons and fermions, relates to their nuclear permutation symmetry, for it is the nuclear motions that exhibit superfluidity. We are thus led to the question: how can fermions (i.e., protons) exhibit many-particle motions that are governed by Bose statistics? We give an answer to this in terms of the Born-Oppenheimer approximation, which does emphasize the very different character of the electronic and nuclear motions.

Thus, in the Born-Oppenheimer approximation, for a collection of H atoms at reasonable pressures we may write the many-body wave function:  $\Psi \cong \Psi_e(\mathbf{r}_i, \mathbf{S}_i, \mathbf{R}_j) \times \Phi_{n,e}(\mathbf{R}_j, \mathbf{I}_j)$ , where  $\Psi_e(\mathbf{r}_i, \mathbf{S}_i, \mathbf{R}_j)$  is the anti-symmetric many-electron spin-orbit wave function for all the electrons in the field of the "clamped" nuclei, whereas  $\Phi_{n,e}(\mathbf{R}_j, \mathbf{I}_j)$  is the many-particle wave function for all the protons in the effective-potential of the electrons in their "ground" electronic state  $\Psi_e$ , and it also includes the nuclear spin-wave-functions. Now the overall require-

ment that  $\Psi$  be antisymmetric with respect to permutation of electrons means that  $\Psi_e$  must have this property. But the overall antisymmetry of  $\Psi$  with respect to permutation of protons is determined not only by  $\Phi_{n,e}$  but by  $\Psi_e$  as well. It is this feature which can allow the protons in the H atoms to exhibit Bose-like behavior.

We first consider  $\Psi_e$ , which can, in general, be written as a sum of one or more Slater determinants. In particular, if we assume a valence-bond type picture, which seems appropriate for H atoms that have not actually recombined, we may write one such Slater determinant in the usual fashion:

$$\Psi_e = (N!)^{-1/2} \parallel \Psi_1(1)\alpha(1), \Psi_2(2)\beta(2), \dots, \Psi_N(N)\beta(N) \parallel \quad (1)$$

where  $\Psi_i(j)$  is the H atom 1s orbital centered on atom  $i$  and it is for electron  $j$ . Equation (1) does not correspond to any particular value of the total electron-spin quantum number  $S_T$ . But, in the spin-aligned state we have  $S_T = N/2$ , and, given this exists only in a very large magnetic field, all electron spins are down; i.e.,  $\Psi_e = \Psi_e^0 \Psi_e^s$ , where  $\Psi_e^s = \prod_{i=1}^N \beta(i)$ , and  $\Psi_e^0 = (N!)^{-1/2} \parallel \Psi_1(1), \Psi_2(2), \dots, \Psi_N(N) \parallel$ , and where the orbital part  $\Psi_e^0$  is itself antisymmetric with respect to electron permutations, but it is also antisymmetric with respect to permutation of nuclear coordinates. Thus, in this spin-aligned state, it immediately follows that  $\Phi_{n,e}(\mathbf{R}_j, \mathbf{I}_j)$  must itself be symmetric with respect to permutations of the protons. Thus, the properties associated with the nuclear motions (in combined space and spin coordinates) would be expected to be those of Bose particles with spin. It also immediately follows, that if we are dealing with spin-aligned deuterium, then  $\Phi_{n,e}(\mathbf{R}_j, \mathbf{I}_j)$  must be antisymmetric with respect to permutations of the deuterons, in order that  $\Psi$  be overall symmetric; so spin-aligned deuterium would behave as fermions.

On the other hand, if the electron spins were not aligned, and, e.g., Eq. (1) applied, then, even though the antisymmetry of the electrons is guaranteed, Eq. (1) does not have any simple symmetry with respect to interchange of nuclear coordinates, because it is not possible to factor out the electron-spin functions. This difficulty can even be seen in the simplest case of  $N = 2!$ <sup>7</sup> Thus, the requirement of overall permutation antisymmetry for the protons would no longer allow for a simple factorization as given above even in the Born-Oppenheimer approximation!

What then is the difference of the spin-aligned H case from that of <sup>4</sup>He, such that in the latter case nuclear bosons lead to the obvious Bose behavior? This is similar to the question of the statistics of hydrogen in its ground state, with  $S_T = 0$ , i.e., hydrogen molecules. In this latter case we can write  $\Psi_e = (N!)^{-1/2} \parallel \Psi_1^{\uparrow}(1)\alpha(1),$

$\Psi_1^m(2)\beta(2), \dots, \Psi_{N/2}^m(N)\beta(N)$  where  $\Psi_1^m(j)$  is the bonding  $\sigma$  molecular orbital at the  $i$ th molecule containing electron  $j$  (while for  $^4\text{He}$  it would be the  $1s$  type orbital). But, in this case (as we have already noted) there are no feasible processes by which the electrons in the separate molecules will exchange over reasonable time scales so the permutation symmetry of such electrons has no practical meaning. In fact, we would assert that the only reasonable processes are just the nuclear motions which exchange well-defined  $\text{H}_2$  molecules. This involves exchange of electron pairs or bosons and proton pairs, again bosons. Thus boson statistics appears quite natural.<sup>6</sup>

We have not, in the above, considered the hyperfine term  $a\mathbf{I} \cdot \mathbf{S}$  in each hydrogen atom, which would tend to couple electron and nuclear spins. If it were important it would tend to invalidate the separation of these spin degrees of freedom as appears above. But, in fact, one requires the presence of very strong magnetic fields which decouple the electron and nuclear spins. Also, it is the residual coupling from  $a\mathbf{I} \cdot \mathbf{S}$  in large but finite magnetic fields (as well as intermolecular spin-dipolar interactions)<sup>3</sup> that act (weakly) to destroy the spin-aligned state with boson-like properties.

Lastly, we wish to call attention to the fact that for the spin-aligned  $H, \Phi_{n,e}(\mathbf{R}_j, \mathbf{I}_j)$  will be nuclear-spin dependent (unless one succeeds in also polarizing the nu-

clear spin-states, a rather severe requirement). However, the usual treatments of the quantum Bose gas are for spinless particles (but see Ref. 3) and this would have to be modified.<sup>8</sup>

<sup>a)</sup>Supported by NSF Grant #CHE 77-26996.

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<sup>5</sup>W. C. Stwalley, Phys. Rev. Lett. **37**, 1628 (1976).

<sup>6</sup>See for example, R. H. Fowler, *Statistical Mechanics*, 2nd ed. (Cambridge, Massachusetts, 1936), pp. 151-155.

<sup>7</sup>In the case of  $N=2$  the singlet state is symmetric with respect to permutation of nuclear coordinates, so  $\Phi_{n,e}$  will obey Fermi statistics. For  $N=4$  there are two singlet states, and they can no longer be simply characterized in terms of nuclear symmetry. The electronic states of definite  $S_T$  can always be written as the appropriate linear combination of Slater determinants.

<sup>8</sup>Modern many-body techniques for composite particles, which could be used for detailed computations on  $\text{H}^+$  are given by M. Girardeau, J. Math. Phys. **16**, 1901 (1975); J. D. Gilbert, J. Math. Phys. **18**, 791 (1977), and references therein.

## Comparison of local-exchange approximations for intermediate-energy electron-molecule differential cross sections

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Local energy-dependent exchange potentials have proved of great value for electron-molecule scattering calculations.<sup>1-31</sup> Although several of the applications have been for low-energy scattering (0-10 eV), the approximations are better justified at intermediate energy and high energy.<sup>32-38</sup> The two most widely used models are the Hara free-electron-gas exchange (HFEGE) approximation<sup>1</sup> and the semiclassical exchange (SCE) approximation,<sup>32</sup> and results obtained with these two models have been directly compared for integral and differential cross sections for  $\text{H}_2$ <sup>23</sup> and for partial and integral cross sections<sup>21,22</sup> and for differential cross sections<sup>27</sup> for  $\text{N}_2$ . The comparison for differential cross sections for  $\text{N}_2$  is that of Siegel *et al.*<sup>27</sup> in the context of the continuum multiple-scattering method<sup>28</sup> with the muffin tin

approximation. In the present note we provide a similar comparison not involving the muffin tin approximation.

We perform converged rigid-rotator rotational close coupling calculations<sup>4</sup> for two different effective potentials. The rotational-orbital basis for each calculation is basis set XVIII-35 of Ref. 11. The effective potentials are identical except for the exchange part. Each potential includes, in addition to exchange, a static potential calculated by the INDOX/1s method<sup>6,10</sup> and a polarization potential calculated by the INDOX/AAP model.<sup>10</sup> The exchange potentials are functionals of electron density, which was obtained by the polarized INDOX/1s method.<sup>10</sup> The resulting rotational-state-to-rotational-state ( $j=0 \rightarrow \text{all } j'$ ) cross sections are given in Table I.