Theory of Small Para-Hydrogen Clusters: Magic Numbers and Superfluid Sizes

S. A. Khairallah, 1 M. B. Sevryuk, 2 D. M. Ceperley, 3 and J. P. Toennies 4

1Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
2Institute of Energy Problems of Chemical Physics RAS, Moscow 119334, Russia
3NCSA and Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
4Max-Planck-Institut für Dynamik und Selbstorganisation, D-37073 Göttingen, Germany

The interplay between magic number stabilities and superfluidity of small para-hydrogen clusters with sizes \( N = 5 \) to 40 and temperatures \( 0.5 \leq T \leq 4.5 \) K is explored with classical and quantum Path Integral Monte Carlo calculations. Clusters with \( N < 26 \) and \( T < 1.5 \) K have large superfluid fractions even at the stable magic numbers 13, 19, and 23. In larger clusters, superfluidity is quenched especially at the magic numbers 23, 26, 29, 32, and 37 while below 1 K, superfluidity is recovered for the pairs (27, 28), (30, 31), and (35, 36). For all clusters superfluidity is localized at the surface and correlates with long exchange cycles involving loosely bound surface molecules.

Hydrogen is the simplest and most ubiquitous of all molecules in the universe. On earth, it plays an important role in many chemical reactions and is presently being developed as an energy transport medium [1]. The \( j = 0 \) rotational state of the para-\( \text{H}_2 \) nuclear spin configuration is, like \( ^4\text{He} \), a spin-less boson and below about 6 K has been predicted to be the only naturally occurring superfluid besides the helium isotopes [2]. The observation of superfluidity in the bulk so far has been thwarted by its solidification at 13.96 K. In 1991, Sindzingre et al. showed theoretically that small pure clusters with 13 and 18 molecules were superfluid below about 2 K, while larger clusters with 33 atoms had a much smaller superfluid fraction [3]. Later, Grebenev et al. observed a superfluid response in small clusters consisting of 15 – 17 para \( \text{H}_2 \) molecules surrounding an OCS chromophore all within a large helium droplet [4]. More recently, Lundström et al. showed theoretically that small pure clusters with 13 and 18 molecules were superfluid below about 2 K, while larger clusters with 33 atoms had a much smaller superfluid fraction [3]. Later, Grebenev et al. observed a superfluid response in small clusters consisting of 15 – 17 para \( \text{H}_2 \) molecules surrounding an OCS chromophore all within a large helium droplet [4]. More recently, Lundström et al. observed a superfluid response in small clusters consisting of 15 – 17 para \( \text{H}_2 \) molecules surrounding an OCS chromophore all within a large helium droplet [4]. More recently, Lundström et al. observed a superfluid response in small clusters consisting of 15 – 17 para \( \text{H}_2 \) molecules surrounding an OCS chromophore all within a large helium droplet [4]. More recently, Lundström et al. observed a superfluid response in small clusters consisting of 15 – 17 para \( \text{H}_2 \) molecules surrounding an OCS chromophore all within a large helium droplet [4].

An intriguing aspect of these studies is the apparent contradiction between the large superfluid fractions and the structured radial distribution functions and the magic number stabilities, which indicate a solid-like rigidity. It is only at high temperatures, when the clusters are molten that the radial distributions show the same constant interior density and smooth fall-off at the surface [3, 6] found for superfluid helium clusters which are known to be liquid [12]. This inconsistency has lead to the speculation that \( \text{pH}_2 \) clusters may be considered as microscopic supersolids [5]. Thus the present study was undertaken to clarify how a cluster which appears to be solid can also be superfluid.

To resolve this apparent incompatibility, both classical and quantum Path Integral Monte Carlo (PIMC) calculations are reported for all sizes between \( N = 5 \) and 40 for 5 temperatures 0.5, 1.0, 1.5, 3.0 K and the experimental accessible 4.5 K [12].

The calculations indicate that clusters with \( N = 13, 19, 23, 26, 29, 32, 34 \) and 37 have highly symmetric structures and show a propensity for stability in agreement with magic number stabilities reported earlier for solid ionized rare gas clusters [14, 15]. In the following, these special sizes will be referred to as magic clusters. All the \( \text{H}_2 \) clusters with \( N < 26 \) have significant superfluid fractions at \( T \leq 1.5 \) K which is only slightly suppressed in the magic clusters. At magic \( N = 26 \), superfluidity is greatly quenched and for \( 29, 32, 34 \) and 37 reduced even down to \( T = 0.5 \) K. Clusters with size pairs (24, 25), (27, 28), (30, 31), the singleton 33, as well as (35, 36) show significantly greater superfluid fractions than their more stable magic neighbours. The radial distributions of the superfluid fraction and the distribution of permutation cycle lengths reveal that superfluidity in all the clusters is localized at the surface and for the larger superfluid sizes, it correlates with the presence of loosely bound surface molecules. These new results now clarify the apparent contradiction between the structured radial distributions and the large superfluidity found in the previous calculations [3, 11].

The calculations were carried using the PIMC method which is based on the quantum-classical isomorphism where each particle is replaced by a polymer made up of M “beads” as explained in detail in reference [10]. In the present quantum calculations a time step of \( \tau = 1/80 \) was sufficient to obtain converged results within the pair-product approximation. Bose statistics is introduced by cross linking the polymers to form chains of permuting cycles (polymers). The classical calculations involve no quantum effects such as permutations and are described in Ref. [17]. Two intermolecular potentials were used: 1) a Lennard-Jones (LJ) potential with parameters \( \sigma = 2.96 \AA \) and \( \epsilon = 34.16 \) K and 2) the more accurate Silvera-Goldman (SG) potential. The initial configurations were chosen either from the Cambridge Cluster Database [18] or by carving out a spherical region centered around a molecule in an hcp \( \text{H}_2 \) crystal. The important effects reported here were independent of the
potential and the initial configuration.

![Graph showing energy differences ∆E as a function of cluster sizes calculated classically (a) and with a quantum mechanical PIMC program (b). The sharp minima marked by downward arrows are attributed to especially stable magic icosahedral-derived structures [14, 15].](image)

FIG. 1: Energy differences ∆E as a function of cluster sizes calculated classically (a) and with a quantum mechanical PIMC program (b). The sharp minima marked by downward arrows are attributed to especially stable magic icosahedral-derived structures [14, 15].

Magic classical and quantum clusters were identified by examining the energy differences ∆E = E(N, T) − E(N − 1, T), where E(N, T) is the total internal energy for a cluster of N molecules at temperature T. ∆E approaches the chemical potential at T = 0, hence sizes with ∆E values lower than their neighbours are more localized and more tightly bound. Both, the classical and the quantum results show about the same enhanced relative stabilities at the magic cluster sizes N = 13, 19, 23, 26, 29, and 32 indicating that the classical stabilities persist in the quantum clusters. Although 36 and 38 appear to be “magic” in the classical simulation, the expected magic 34 and 37, are found only in the quantum calculations [14, 15]. All our quantum calculated magic numbers agree with well-known high symmetry icosahedral-derived structures [14] and have been repeatedly observed in ionized rare gas clusters [14, 15]. So far, however, only magic N = 13, 33 and 55, have been observed experimentally [5]. Whereas N = 13 and 55 correspond to the closing of the first and second icosahedral shells, N = 33 is not a magic number among the possible modified icosahedral structures but has a dodecahedral form. Since the experimental resolution [5] was not sufficient to distinguish from the nearby magic 32 and 34, it is possible that the earlier assignment may be incorrect. Especially if one considers that during cluster growth icosahedral modified structures will be preferred as a result of build-up around the smallest magic N = 13 which will be a nucleus for further growth.

The superfluid fraction ρs/ρtotal [10] is shown in Fig.2 as a function of cluster size and temperature. The nearly 100% fraction in the small clusters decreases sharply above 1.5 K [14]. At each of the magic sizes ρs/ρtot almost always shows a downward dip reminiscent of those in Fig. 1. These dips are smallest in the small clusters but are more pronounced for N ≥ 26. Thus, the classical rigidity at the magic sizes suppresses the quantum delocalization needed for superfluidity, an effect which becomes stronger with increasing size. Surprisingly, beyond magic N = 23, the superfluid fraction at 1 K jumps back to about unity for the next larger sizes (24, 25). Then beyond magic N = 26 a similar rebound occurs for the two lowest temperatures at (27, 28). The minimum at N = 23 and two maxima at N = 25, 27 were also found in recent calculations by Mezzacapo and Bonisegni [11]. In the present calculations similar maxima are found at (30, 31), and (35, 36). The singleton N = 33 has a very weak rebound and seems to follow the behaviour of the neighbouring magic sizes as its relatively low binding energy in Fig.1(b) also suggests. Thus in clusters with solid-like stable structures superfluidity is suppressed, with the largest suppressions found for N ≥ 26, while at sizes not corresponding to known magic sizes, it is restored. It is interesting to note that at 1.5 K the interactions are so strong that superfluidity is almost suppressed for clusters N ≥ 26, yet quantum delocalization in the smaller clusters is still sufficient for their superfluidity.

To understand these unexpected out-of-phase oscillations between magic sizes and superfluid sizes the three types of radial distributions shown in Fig.3 were calculated for the magic N = 26 cluster and the two adjacent less stable but more superfluid clusters. Fig.3 (a) shows the classical distributions at 1.5 K. As expected classically(Fig.3(a)), the molecules in N = 26 follow an orderly partitioning into four localised and distinct groups, whereas for N = 25, 27 they are randomly distributed. The quantum distributions (Fig.3b) with only two broad peaks show evidence of quantum exchanges between the shells. The magic N = 26 cluster has a noticeably larger inner peak compared to its neighbors and also shows a
The superfluidity is small in the inner shell specially for 
the outer maximum in the radial density distribution.
4
perfluidity is not greatest near the center as found for
the nature of the disorder favouring a large superfluid
fraction at the surface emerges from the “inherent struc-
ture” (IS) analysis of Stillinger and Weber [21]: “inherent structures which underlie the liquid state are those sta-
ble particle packings (potential minima) which can be
reached by a steepest descent quench on the potential
s
Fig. 2). Contours at
different values of z for larger clusters at T \geq 1.5 K (not
shown) show similar localization. The corresponding per-
mutation probabilities are peaked at very low cycle num-
bers and are mostly less than 0.05%, which explains their
small residual superfluidity in Fig. 2. But as shown by
the permutation probabilities even the magic N = 26
melts and become superfluid at 0.5 K with a predomi-
nance of cycles from 7 to 15. The top panel in Fig. 4
for non-magic N = 27 has a liquid outer layer similar to
magic 13 in agreement with Fig. 3(c) but with a smaller
peak permutation probability of about 3.5% as expected
from its small overall superfluid fraction (Fig. 2). At
0.5 K the permutation probability curve smoothens and
extends out to include cycles equal to 27 suggesting that
also the core molecules are participating in the permuta-
tions. Thus both the contour plots and probability
distributions of the N = 27 cluster are consistent with
the onset of superfluidity in the surface region.

Recently, Mezzacapo and Boninsegni also observed an
enhanced superfluidity for N = 25, but their conclusion
that “the addition of a molecule to the N + 1 = 26 has
the effect of frustrating the solid order of the inner shell,
increasing molecule delocalization and leading to quan-
tum exchanges” [11] is at variance with these new results,
which clearly show that superfluidity is at the surface.

The surface molecules in N = 27 cluster at 1 K are highly
delocalized, whereas the core molecules are nearly rigid. This
 correlates with the long exchange paths around the localized
core shown below the contour plot.

Additional insight comes from Fig. 4 which provides a
cross section view of N = 13, 26 and 27 and the proba-
bility distributions of the permutation cycles as a function of
the permutation lengths. The contours for N = 13 show a considerable delocalization of the outer layer. The
N = 13 permutation probabilities are dominated by cy-
cles with lengths of 5 and 6 molecules, corresponding to
rings around the center, with a relatively high probability
of 10% in accordance with the large superfluid fraction
(Fig. 2). Even though the central molecule appears to be
localized in the contour plot at 0.5 K, it also participates
in ring exchanges as indicated by the small \approx 0.1% prob-
ability for cycle exchange lengths of 13. The contour
plot for magic N = 26 indicates that all its molecules are
highly localized and that it is solid-like justifying the
greatly suppressed superfluidity (Fig. 2). Contours at

slight dimple in the second outermost peak reminiscent
of the classical distribution. The radial dependence of
the superfluid fraction \rho_s(r)/\rho [20] in Fig. 3(c) is com-
puted by binning the radial location of the beads that are
involved in permutation cycles [20]. These distributions exhibit large differences with temperature and with
sizes as expected from Fig. 2. Surprisingly, however, su-
perfluidity is not greatest near the center as found for
He clusters [12], but is localized at the surface beyond
the outer maximum in the radial density distribution.
The superfluidity is small in the inner shell specially for
magic N = 26. We note that the apparent randomness in
the classical radial curves (Fig. 3(a)), which is suggestive
of less rigid and symmetric structures for the non-magic
N = 25 and 27, correlates with the increased superfluid
fractions (Fig. 3(c) and Fig. 2).

The recent addition of a molecule to the N + 1 = 26 has
the effect of frustrating the solid order of the inner shell,
increasing molecule delocalization and leading to quan-
tum exchanges [11] is at variance with these new results,
which clearly show that superfluidity is at the surface.

The nature of the disorder favouring a large superfluid
fraction at the surface emerges from the “inherent struc-
ture” (IS) analysis of Stillinger and Weber [21]: “inherent structures which underlie the liquid state are those sta-
ble particle packings (potential minima) which can be
reached by a steepest descent quench on the potential

FIG. 3: Comparison of radial density distributions for the
magic cluster N = 26 and the neighbours (25, 27) for three
characteristic temperatures. The distributions in (a) are clas-
sical and those in (b) are from quantum calculations. The
radial distribution of the superfluid fraction is plotted in (c).
We show one temperature in (a) since the classical distribu-
tions are less sensitive to temperature.
energy hypersurface”. This quenching procedure eliminates all kinetic effects due to thermal excitations or zeropoint motion. To generalize this concept to quantum mechanical systems, in the steepest descent minimization, the gradient was calculated from the path integral action rather than from the potential. The permutations were turned off and the IS analysis was applied to “Boltzmanns”. The quenched structures are, in general, independent of the temperature \( T \) and are identical to Wales classical minimum potential energy configurations \([18]\). This geometric spatial correspondence explains the origin of the persistence of the classical structures in the energy and superfluid densities discussed above.

Among the small cluster sizes, a quenched configuration similar to the Wales body centered icosahedron was quite often found for \( N = 13 \) indicating that it is particularly stable. Occasionally, quenching would generate variant structures close to the classical ones with some delocalized molecules on the surface suggestive of melting. Clusters differing by one or two molecules from the magic sizes are more often seen to have defective surfaces. Since these clusters differ essentially only in the bonding of the outer molecules, their smaller binding energies (Fig 2) indicate that these outer molecules are less tightly bound than in the case of the magic clusters. For example, \( N = 18 \) would statistically appear more often with structures that deviate slightly from the classical clusters, while for magic \( N = 19 \), almost every IS cluster is the same as the classical cluster. The IS analysis for the other larger superfluid sizes indicates that their surface molecules are also less tightly bound and less ordered.

In summary, our analysis reveals that pure \( pH_2 \) clusters with \( N < 26 \) at temperatures \( T < 1.5K \) are liquid-like and have a large superfluid response. It is only somewhat reduced in magic clusters \( N = 13, 19 \) and 23, which are classical magic sizes with highly symmetric icosahedral structures. According to Fig 1 (b), the difference in internal energies, which is the energy needed to add one molecule, is less than \( 38K \) for these highly superfluid clusters. The larger magic clusters \( N = 26, 29, 32, 34, \) and 37, in which superfluidity is strongly quenched at temperatures \( T > 0.5K \), all have considerably larger internal energy differences of more than about \( 40K \). Superfluidity is restored in the cluster size pairs \( N = (24,25), (27,28), (30,31), \) the singleton 33, and (35,36), with smaller internal energy differences compared to the magic clusters which lie in between. In these superfluid sizes, quantum delocalization of the loosely bound ad-molecules enables them to explore many different surface structures, thereby favouring large permutation cycles and an increased superfluidity. Our calculations reveal that with increasing cluster size the strong many-body intermolecular interactions lead to a rigid solid-like inner core thereby pushing the delocalization induced superfluidity towards the surface, where it is favored by the reduced coordination and weak inward interaction with the small central core. The overall decay of superfluidity with cluster size and its increased localization on the surface agrees with the macroscopic limit of 2D surface superfluidity and zero response in the bulk \([22]\).

We thank Dr.Oleg A. Kornilov and Prof. L. Yu Rusin for helpful discussions and Prof. Victoria Buch for her classical code. This work was supported by NSF(DMR-04-04853), NASA (NAG-8-1760) and the Deutsche-Forschungsgemeinschaft. Computer time was provided by NCSA, the F. Seitz Materials Research Lab. (US DOE DEFG02-91ER45439 and NSF DMR-03 25939 ITR) at the U. of Illinois Urbana-Champaign.

\[\text{References}\]

1. \[\text{http://www.eere.energy.gov/hydrogenandfuelcells/}\]
2. V. L. Ginzburg and A. A. Sobyanin, JETPLetters 15(6) 343 (1972).
3. P. Sindzingre, D. M. Ceperley, and M. L. Klein, Phys. Rev. Lett., 67, 1871-1874 (1991)
4. S. Grebenev, B. Sarkakov, J. P. Toennies, A. F. Vilesov, Science, 289(5484), 1532 - 1535 (2000).
5. G. Tejeda J. M. Fernández, S. Montero, D. Blume, J. P. Toennies, Phys. Rev. Lett., 92(22), 224301 (2004).
6. D. Scharf, G. J. Martyna, M. L. Klein, Chem. Phys. Lett., 197(3), 231 - 235 (1992).
7. Y. Kwon, K. B. Whaley, Phys. Rev. Lett., 89, 273401 - 1 (2002).
8. S. Baroni, S. Moroni, Chem. Phys. Chem., 6(9), 1884-1888 (2005).
9. J. E. Cuervo, P. N. Roy, J. Chem. Phys. 125, 124314 (2006).
10. R. Guardiola, J. Navarro. Phys. Rev. A74, 025201 (2006).
11. F. Mezzacapo, M. Boninsegni, Phys. Rev. Lett., 97(4), 045301 (2006). F. Mezzacapo, M. Boninsegni, cond-mat/ 0611775.
12. P. Sindzingre, M. L. Klein, and D. M. Ceperley, Phys. Rev. Lett., 63, 1601 (1989)
13. E. L. Knuth, F. Schneemann, and J. P. Toennies, J. Chem. Phys. 102, 6258 (1995).
14. J. Farges, M. F. de Ferandy, B. Raoul and G. Torchet, Surface Science, 156, 370 (1985).
15. W. Miehle, O. Kandler, T. Leisner and O. Echt, J. Chem. Phys., 91, 5940 (1989).
16. D. M. Ceperley.Rev.Modern Phys., 67(2),279-355 (1995).
17. V. Buch, J.Chem.Phys.,100(10),7610-7629 (1994).
18. \[\text{http://www-doye.ch.cam.ac.uk/jon/structures /LJ/tables.150.html.}\] D. J. Wales, J. P. Doye, J.Phys.Chem. A,101(28),5111-5116 (1997).
19. Values greater than 100% in Fig.2 result from ambiguity in the definition of the moments of inertia in small clusters.
20. E. W. Draeger, D. M. Ceperley, Phys.Rev.Lett.90, 065301 2003.
21. T. A. Weber, F. H. Stillinger, J. Chem. Phys., 81(11), 5089-5094 (1984).
22. M. Wagner, D. M. Ceperley, J. Low Temp. Phys. 94, 147 (1994).