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Chierigato, A.a c , Ochoa, J.V.a , Bandinelli, C.a d , Fornasari, G.a , Cavani, F.a c d , Mella, M.b

On the chemistry of ethanol on basic oxides: Revising mechanisms and intermediates in the lebedev and guerbet reactions

(2015) ChemSusChem, 8 (2), pp. 377-388.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84920871061&partnerID=40&md5=38db90270473e314daacf799b7bc49b1>

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ABSTRACT: A common way to convert ethanol into chemicals is by upgrading it over oxide catalysts with basic features; this method makes it possible to obtain important chemicals such as 1-butanol (Guerbet reaction) and 1,3-butadiene (Lebedev reaction). Despite their long history in chemistry, the details of the close inter-relationship of these reactions have yet to be discussed properly. Our present study focuses on reactivity tests, in situ diffuse reflectance infrared Fourier transform spectroscopy, MS analysis, and theoretical modeling. We used MgO as a reference catalyst with pure basic features to explore ethanol conversion from its very early stages. Based on the obtained results, we formulate a new mechanistic theory able to explain not only our results but also most of the scientific literature on Lebedev and Guerbet chemistry. This provides a rational description of the intermediates shared by the two reaction pathways as well as an innovative perspective on the catalyst requirements to direct the reaction pathway toward 1-butanol or butadiene.

AUTHOR KEYWORDS: Alcohols; Alkenes; Density functional calculations; Magnesium; Reaction mechanisms

DOCUMENT TYPE: Article

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Chierigato, A.a c e , VelasquezOchoa, J.a e , Bandinelli, C.a d , Fornasari, G.a , Cavani, F.a c d , Mella, M.b

On the Chemistry of Ethanol on Basic Oxides: Revising Mechanisms and Intermediates in the Lebedev and Guerbet reactions

(2015) ChemSusChem, . Article in Press.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84920567166&partnerID=40&md5=d06309825e57cb50e4bbf329e0b9f9ec>

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ABSTRACT: A common way to convert ethanol into chemicals is by upgrading it over oxide catalysts with basic features; this method makes it possible to obtain important chemicals such as 1-butanol (Guerbet reaction) and 1,3-butadiene (Lebedev reaction). Despite their long history in chemistry, the details of the close inter-relationship of these reactions have yet to be discussed properly. Our present study focuses on reactivity tests, in situ diffuse reflectance infrared Fourier transform spectroscopy, MS analysis, and theoretical modeling. We used MgO as a reference catalyst with pure basic features to explore ethanol conversion from its very early stages. Based on the obtained results, we formulate a new mechanistic theory able to explain not only our results but also most of the scientific literature on Lebedev and Guerbet chemistry. This provides a rational description of the intermediates shared by the two reaction pathways as well as an innovative perspective on the catalyst requirements to direct the reaction pathway toward 1-butanol or butadiene.

AUTHOR KEYWORDS: Alcohols; Alkenes; Density functional calculations;

Magnesium; Reaction mechanisms
DOCUMENT TYPE: Article in Press
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Mella, M.a , Cargnoni, F.b

Exciplexes with ionic dopants: Stability, structure, and experimental relevance of $M+(2P)4He_n$ ($M = Sr, Ba$)

(2014) Journal of Physical Chemistry A, 118 (33), pp. 6473-6483.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84906502900&partnerID=40&md5=570710df07a3d779059f04f4f243594c>

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ABSTRACT: $M+(2P)4He_n$ species, possibly involved in the post $2P \leftarrow 2S$ excitation dynamics of Sr^+ and Ba^+ in cold $4He$ gas or droplets, are studied employing both high level ab initio calculations to determine the potential energy curves (PEC) and diffusion Monte Carlo (DMC) to obtain information on their ground state structure and energetics. PEC for the excited $M+(2P)He$ dimers were obtained using MRCI calculations with extended basis sets. Potential energy surfaces (PES) for $M+(2P)He_n$ were built with the DIM model including spin-orbit coupling via a perturbative procedure. DMC simulations indicated several exciplexes ($n \geq 2$) to be stable against He dissociation whatever the ion state, a finding that is at variance with what was previously suggested for $Ba+(2P_{1/2})$ due to the repulsive nature of the interaction potential obtained in [Phys. Rev. A 2004, 69, 042505]. Our results, instead, support the suggestion made in [J. Chem. Phys. 2012, 137, 051102] for the existence of $Ba+(2P_{1/2})He_n$ exciplexes emitted following the excitation of the barium cation solvated into He droplets. In the $2P_{1/2}$ state, the Ba ion also shows a peculiar behavior as a function of n with respect to the location and binding strength of the attached He atoms compared to Sr^+ . Although the latter forms the usual equatorial He ring, Ba^+ deviates from this geometry for $1 \leq n \leq 4$, with the radial distribution functions strongly depending on the number of solvent atoms. Finally, a putative species is proposed to explain the emission band at 523 nm that follows D_1 or D_2 excitation of Ba^+ in superfluid bulk helium. © 2014 American Chemical Society.

DOCUMENT TYPE: Article

SOURCE: Scopus

Wolf, S.a , Curotto, E.a , Mella, M.b

Quantum monte carlo methods for constrained systems

(2014) International Journal of Quantum Chemistry, 114 (10), pp. 611-625. Cited 1 time.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84897572850&partnerID=40&md5=696ef5542dde7ef3a719d0883f3134c8>

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ABSTRACT: The torsional ground state for ethane, the torsional, rotational, and mixed torsional and rotational ground state of propane are computed with a version of diffusion Monte Carlo adapted to handle the geometric complexity of curved spaces such as the Ramachandra space. The quantum NVT ensemble average for the mixed torsional and rotational degrees of freedom of propane is computed, using a version of Monte Carlo path integral, also adapted to handle curved spaces. These three problems are selected to demonstrate the generality and the applicability of the approaches described. The spaces of coordinates can be best constructed from the parameters of continuous Lie groups, and alternative methods based on vector spaces, where extended Lagrangian terms would be too cumbersome to implement. We note that the geometric coupling between the torsions and the rotations of propane produces a substantial effect on the ground state energy of propane, and that the quantum effects on the energy of propane are quite large even well above room temperature. Copyright © 2014 Wiley Periodicals, Inc.

AUTHOR KEYWORDS: diffusion Monte Carlo; Holonomic constraints; path integral

Monte Carlo; quantum Monte Carlo; Ramachandra space
DOCUMENT TYPE: Review
SOURCE: Scopus

Mateo, D.a , Leal, A.a , Hernando, A.b , Barranco, M.a , Pi, M.a , Cargnoni, F.c , Mella, M.d , Zhang, X.e , Drabbels, M.e

Communication: Nucleation of quantized vortex rings in 4He nanodroplets
(2014) Journal of Chemical Physics, 140 (13), art. no. 4870245, . Cited 4 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-84898016231&partnerID=40&md5=c1b305f6bf6a5006e78711d100a42c8c>

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ABSTRACT: Whereas most of the phenomena associated with superfluidity have been observed in finite-size helium systems, the nucleation of quantized vortices has proven elusive. Here we show using time-dependent density functional simulations that the solvation of a Ba⁺ ion created by photoionization of neutral Ba at the surface of a 4He nanodroplet leads to the nucleation of a quantized ring vortex. The vortex is nucleated on a 10 ps timescale at the equator of a solid-like solvation structure that forms around the Ba⁺ ion. The process is expected to be quite general and very efficient under standard experimental conditions. © 2014 AIP Publishing LLC.

DOCUMENT TYPE: Article

SOURCE: Scopus

Curotto, E.a , Mella, M.b

Infinite swapping in curved spaces

(2014) Journal of Chemical Physics, 140 (1), art. no. 014103, . Cited 1 time.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-84891876831&partnerID=40&md5=45aeb5e2e6ff9b72ebca8c5596b60173>

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ABSTRACT: We develop an extension of the infinite swapping and partial infinite swapping techniques [N. Plattner, J. D. Doll, P. Dupuis, H. Wang, Y. Liu, and J. E. Gubernatis, J. Chem. Phys. 135, 134111 (2011)] to curved spaces. Furthermore, we test the performance of infinite swapping and partial infinite swapping in a series of flat spaces characterized by the same potential energy surface model. We develop a second order variational algorithm for general curved spaces without the extended Lagrangian formalism to include holonomic constraints. We test the new methods by carrying out NVT classical ensemble simulations on a set of multidimensional toroids mapped by stereographic projections and characterized by a potential energy surface built from a linear combination of decoupled double wells shaped purposely to create rare events over a range of temperatures. © 2014 AIP Publishing LLC.

DOCUMENT TYPE: Article

SOURCE: Scopus

Pasini, T.a b , Lolli, A.a b , Albonetti, S.a b , Cavani, F.a b , Mella, M.c
Methanol as a clean and efficient H-transfer reactant for carbonyl reduction: Scope, limitations, and reaction mechanism

(2014) Journal of Catalysis, 317, pp. 206-219. Cited 1 time.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84905592281&partnerID=40&md5=d0fa4eafc9cf2326c3a4515bbdb25a8b>

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ABSTRACT: The previously unexplored use of methanol as a H-transfer agent for the Meerwein-Ponndorf-Verley reduction of aromatic aldehydes and aryl ketones is described. Furfural, 5-hydroxymethylfurfural, benzaldehyde, and acetophenone were selectively reduced to the corresponding alcohols in mild conditions. The reaction mechanism was elucidated by means of reactivity tests and DFT calculations. It was found to include the highly efficient H-transfer with the formation of formaldehyde, which further reacted with excess methanol to generate the adsorbed hemiacetal. In turn, the latter reduced carbonyl, with the formation of methylformate, which further decomposed into CO, CH₄, and CO₂. Compared to the alcohols typically used for carbonyl reductions, methanol showed the advantage of producing gaseous components as the only co-products, which are easily separated from the reaction medium. In the case of furfural, a 100% yield to furfuryl alcohol was obtained, using the high-surface area MgO as the easily recoverable and reusable catalyst. © 2014 Elsevier Inc. All rights reserved.

AUTHOR KEYWORDS: 5-Hydroxymethylfurfural; Furfural; Hydrogen transfer; Meerwein-Ponndorf-Verley reduction; Methanol; MgO

DOCUMENT TYPE: Article

SOURCE: Scopus

Jenkins, R.a , Curotto, E.a , Mella, M.b

Replica exchange with Smart Monte Carlo and Hybrid Monte Carlo in manifolds (2013) *Chemical Physics Letters*, 590, pp. 214-220. Cited 1 time.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84890122281&partnerID=40&md5=6599ad04762d2e2a2264a216e7929d60>

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ABSTRACT: Several Smart Monte Carlo (SMC) and Hybrid Monte Carlo (HMC) simulations coupled with the Replica Exchange (RE) strategy are compared in multidimensional flat and curved manifolds characterized by extremely rugged potential energy surfaces, to quantify their convergence properties with respect to walk length and overall cost. We learn that the HMC coupled with a sampling enhancing method is much more efficient in manifolds mapped with unconventional coordinates than SMC. This is due to an inherent difficulty in conserving energy in curved spaces directly mapped, and the lack of such strict requirement for HMC. © 2013 Elsevier B.V. All rights reserved.

DOCUMENT TYPE: Article

SOURCE: Scopus

Cargnoni, F.a , Ponti, A.a , Mella, M.b

Coinage metal exciplexes with helium atoms: A theoretical study of M*(2L)He_n (M = Cu, Ag, Au; L = P, D)

(2013) *Physical Chemistry Chemical Physics*, 15 (42), pp. 18410-18423. Cited 3 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84885640369&partnerID=40&md5=00580c2a37a34e6be12b49780b61a92b>

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ABSTRACT: The structure and energetics of exciplexes M*(2L)He_n (M = Cu, Ag and Au; L = P and D) in their vibrational ground state are studied by employing diffusion Monte Carlo (DMC). Interaction potentials between the excited coinage metals and He atoms are built using the Diatomics-in-Molecule (DIM) approach and ab initio potential curves for the M(2L)-He dimers. Extending our previous work [Cargnoni et al., *J. Phys. Chem. A*, 2011, 115, 7141], we computed the dimer potential for Au in the 2P and 2D states, as well for Cu and Ag in the 2D state, employing basis set superposition error-corrected Configuration Interaction calculations. We found that the 2Π potential correlating with the 2P state of Au

is substantially less binding than for Ag and Cu, a trend well supported by the M^+ ionic radiuses. Conversely, the interaction potentials between a $(n-1)d^9 ns^2$ 2D metal and He present a very weak dependency on M itself or the projection of the angular momentum along the dimer axis. This is due to the screening exerted by the ns^2 electrons on the hole in the $(n-1)d$ shell. Including the spin-orbit coupling perturbatively in the DIM energy matrix has a major effect on the lowest potential energy surface of the 2P manifold, the one for Cu allowing the formation of a "belt" of five He atoms while the one for Au being completely repulsive. Conversely, spin-orbit coupling has only a weak effect on the 2D manifold due to the nearly degenerate nature of the diatomic potentials. Structural and energetic results from DMC have been used to support experimental indications for the formation of metastable exciplexes or the opening of non-radiative depopulation channels in bulk and cold gaseous He. © 2013 the Owner Societies.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Curotto, E.b

Quantum simulations of the hydrogen molecule on ammonia clusters

(2013) Journal of Chemical Physics, 139 (12), art. no. 124319, . Cited 2 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84903362121&partnerID=40&md5=cc7c7c7dbd2dfd79247997d88488a6e151d>

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ABSTRACT: Mixed ammonia-hydrogen molecule clusters $[H_2-(NH_3)_n]$ have been studied with the aim of exploring the quantitative importance of the H_2 quantum motion in defining their structure and energetics. Minimum energy structures have been obtained employing genetic algorithm-based optimization methods in conjunction with accurate pair potentials for NH_3-NH_3 and H_2-NH_3 . These include both a full 5D potential and a spherically averaged reduced surface mimicking the presence of a para- H_2 . All the putative global minima for $n \geq 7$ are characterized by H_2 being adsorbed onto a rhomboidal ammonia tetramer motif formed by two double donor and two double acceptor ammonia molecules. In a few cases, the choice of specific rhombus seems to be directed by the vicinity of an ammonia ad-molecule. Diffusion Monte Carlo simulations on a subset of the species obtained highlighted important quantum effects in defining the H_2 surface distribution, often resulting in populating rhomboidal sites different from the global minimum one, and showing a compelling correlation between local geometrical features and the relative stability of surface H_2 . Clathrate-like species have also been studied and suggested to be metastable over a broad range of conditions if formed. © 2013 AIP Publishing LLC.

DOCUMENT TYPE: Article

SOURCE: Scopus

Izzo, L.a , Mella, M.b

Interpreting "acidity" as a global property controlling comonomer reactivity in olefin polymerization

(2013) Organometallics, 32 (11), pp. 3192-3202.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84878874645&partnerID=40&md5=052d06bedf2e104baf43c2897c5f365a>

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ABSTRACT: A possible rationale for the different catalytic behaviors of systems based on *rac*-(ethylenebis(1-indenyl))zirconium dichloride (*rac*-EBIZrCl₂), *rac*-(ethylenebis(1-indenyl))hafnium dichloride (*rac*-EBIHfCl₂), and *rac*-(isopropylidenebis(1-indenyl))zirconium dichloride (*rac*-iPrBIZrCl₂) toward ethene-styrene copolymerization has been sought by studying related active systems. For this purpose, the metallocene ion pairs (IPs) *rac*-EBIZrMe - MeB(C₆F₅)₃, *rac*-EBIHfMe - MeB(C₆F₅)₃, and *rac*-iPrBIZrMe - MeB(C₆F₅)₃ have been synthesized and their structures in solution explored with ROESY and pulsed

gradient NMR spectroscopy. The energetics of dynamical processes relevant for catalysis that can be used as indicators of the cation acidity have been studied with variable-temperature NMR experiments and density functional theory (DFT). NMR experiments successfully provided IP structural details in solution and also indicated the presence of an intricate dynamic behavior for all the IPs. DFT results, instead, indicated quantitatively how changing the metal and/or the ancillary ligand bridge influences the energetics of the active species and modifies the reaction energy profile. The theoretical results also drew attention to the fact that finding a rationale for the ligand influence on the catalytic behavior of *rac*-EBIZrCl₂/MAO and *rac*-iPrBIZrCl₂/MAO in ethene-styrene copolymerization requires not only considering the steric effects but also determining how subtle changes in the ligand sphere affect the capability of the metal center to accept electrons from the counteranion or the olefins. © 2013 American Chemical Society.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.

Exploring unvisited regions to investigate solution properties: The backyard of H₃O⁺ and its aggregates

(2013) Chemical Physics Letters, 555, pp. 51-56.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84871366411&partnerID=40&md5=7f7ebc408c356392894a301803379c04>

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ABSTRACT: Interactions between bare and tri-solvated (Eigen) hydronium with water and methanol is investigated with ab initio methods. Unexplored configurations on the oxygen side of H₃O⁺ are covered to improve our understanding of the solvation energetics. Results indicate that the interaction between the charged and polar species, with oxygen atoms oriented toward H₃O⁺ oxygen ('back to back' or 'O-side' to 'O-side' interaction), is similar to or stronger than a hydrogen bond. The repulsion along the O-O directrix onset in the range 2.2-2.7, indicating H₂O short-range O-O contacts with (H₃O⁺) as possible despite water coordination. © 2012 Elsevier B.V. All rights reserved.

DOCUMENT TYPE: Article

SOURCE: Scopus

Unn-Toc, W.a , Halberstadt, N.a , Meier, C.a , Mella, M.b c

Exploring the importance of quantum effects in nucleation: The archetypical Ne_n case

(2012) Journal of Chemical Physics, 137 (1), art. no. 014304, . Cited 1 time.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84863693038&partnerID=40&md5=bb43139f5eb56a0d09fa296a7fba2be2>

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ABSTRACT: The effect of quantum mechanics (QM) on the details of the nucleation process is explored employing Ne clusters as test cases due to their semi-quantal nature. In particular, we investigate the impact of quantum mechanics on both condensation and dissociation rates in the framework of the microcanonical ensemble. Using both classical trajectories and two semi-quantal approaches (zero point averaged dynamics, ZPAD, and Gaussian-based time dependent Hartree, G-TDH) to model cluster and collision dynamics, we simulate the dissociation and monomer capture for Ne₈ as a function of the cluster internal energy, impact parameter and collision speed. The results for the capture probability P_s(b) as a function of the impact parameter suggest that classical trajectories always underestimate capture probabilities with respect to ZPAD, albeit at most by 15-20 in the cases we studied. They also do so in some important situations when using G-TDH. More interestingly, dissociation rates k_{diss} are grossly overestimated by classical mechanics, at least by one order of magnitude. We interpret both behaviours as mainly due to the reduced

amount of kinetic energy available to a quantum cluster for a chosen total internal energy. We also find that the decrease in monomer dissociation energy due to zero point energy effects plays a key role in defining dissociation rates. In fact, semi-quantal and classical results for k_{diss} seem to follow a common corresponding states behaviour when the proper definition of internal and dissociation energies are used in a transition state model estimation of the evaporation rate constants. © 2012 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Shepppleman Jr., J.P.^a, Smizaski, G.W.^a, Curotto, E.^a, Mella, M.^{b c}
An analytical potential energy model for ammonia-H₂ from first principle
(2012) Chemical Physics Letters, 535, pp. 49-55. Cited 1 time.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84860270080&partnerID=40&md5=5affd956d22e3e6dceaa6f6c0609c073>

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ABSTRACT: We construct a set of analytical potential energy models for the interaction of the para-H₂-ammonia, ortho-H₂-ammonia, and classical-H₂-ammonia dimers by fitting a function to a number of ab initio energies. The minimum energy for the classical-H₂-ammonia dimer is at -1.1164 mhartree. The classical-H₂ molecule is the 'hydrogen bond donor' on the side of the lone pair on the nitrogen atom. The minimum energy obtained for the para-H₂-ammonia is -0.289 mhartree, and for ortho-H₂-ammonia is -0.281 mhartree. The ammonia molecule is the hydrogen bond donor in both dimers. © 2012 Elsevier B.V. All rights reserved.

DOCUMENT TYPE: Article

SOURCE: Scopus

Vigliotta, G.^a, Mella, M.^{c d}, Rega, D.^a, Izzo, L.^{a b}

Modulating antimicrobial activity by synthesis: Dendritic copolymers based on nonquaternized 2-(dimethylamino)ethyl methacrylate by Cu-mediated ATRP
(2012) Biomacromolecules, 13 (3), pp. 833-841. Cited 9 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-84858118437&partnerID=40&md5=53bd763bc09e02ef74ee9fc593c66a4c>

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ABSTRACT: The synthesis of novel star-like heteroarms polymers A(BC)_n containing m-PEG (block A), methylmethacrylate (MMA), and nonquaternized 2-(dimethylamino)ethyl methacrylate (DMAEMA) (blocks BC) is here reported. We demonstrated that copolymer films with comparable amounts of DMAEMA have antimicrobial properties strongly depending on the topological structure (i.e., the number of arms) of the composing copolymers. We interpret the highest antimicrobial activity of A(BC)₂ with respect to A(BC)₄ and linear copolymers (respectively, A(BC)₂ > A(BC)₄ > A(BC)) as probably due to the formation of strong hydrogen bonds between close amino-ammonium groups in the A(BC)₂ film. Strong hydrogen bonds seem to be somewhat disfavored in the case of the linear species by the difference in both polymer architecture and film morphology compared with the A(BC)₂ and A(BC)₄ architectures. © 2012 American Chemical Society.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.^{a b}, Izzo, L.^c, Capacchione, C.^c

Role of the metal center in the ethylene polymerization promoted by group 4

complexes supported by a tetradentate [OSSO]-type Bis(phenolato) ligand
(2011) ACS Catalysis, 1 (11), pp. 1460-1468. Cited 5 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-80655138677&partnerID=40&md5=6befbd3a6fd99d8a12579ca369bee519>

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ABSTRACT: The mechanism responsible for the production of branched polyethylene from ethylene feed during its polymerization promoted by dichloro{1,4-dithiabutanediyl-2,2'-bis(4,6-di-tert-butyl-phenoxy)}titanium complex 1 activated by methylalumoxane (MAO) was investigated by using a density functional theory (DFT) approach. The following processes, chain propagation (CP) reaction, beta hydrogen elimination (β HE, hydrogen elimination from an alkyl chain to the metal in the absence of a coordinated alkene) and transfer (β HT, hydrogen transfer from the alkyl chain to a coordinated alkene) were considered to individuate the possible competing reactions responsible for the production of ethylene oligomers. The latter two processes are generally ascribed as termination reactions for the chain propagation. We found that β HT is the more plausible termination pathway leading to the formation of oligomers that can be reinserted in the growing chain, and thus giving the branched polyethylene. Furthermore, by comparing the energetic profile of CP and β HT for the analogue zirconium compound 2 we found that β HT is 50 times more competitive with CP than for the Ti-based compound. As a matter of fact, the MAO activated zirconium complex exclusively produces oligomers with even number of carbon atoms, thus confirming fairly well the calculations that indicated the possibility of tuning the catalytic activity and selectivity of this class of compounds simply by changing the nature of the metal center. © 2011 American Chemical Society.

AUTHOR KEYWORDS: DFT calculations; ethylene oligomerization; postmetallocene; titanium; zirconium

DOCUMENT TYPE: Article

SOURCE: Scopus

Karabulut, S.a , Namli, H.a , Mella, M.b

Detection of relative dimer and rotamer concentrations of diacetamide in different solvents by FT-IR spectroscopy and DFT calculations
(2011) Vibrational Spectroscopy, 57 (2), pp. 294-299. Cited 2 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-80054727858&partnerID=40&md5=509fd1c57d7e092803a85e11049b0cde>

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ABSTRACT: The relative rotamer, dimer and tautomer concentrations of diacetamide have been studied by means of infrared spectroscopy, with the recorded spectra being analyzed employing results from density functional theory calculations. It is observed that the cis-trans monomeric form of diacetamide (1) is found to be the most stable isomer in all studied solvents, with trans-trans diacetamide (2) being found to be 20% of total diacetamide in methanol. While the dimer form of diacetamide (3) is present only in carbontetrachloride (about 34% of the total), its tautomeric forms (4, 5) are not favorable in any of the studied solvents. © 2011 Elsevier B.V.

AUTHOR KEYWORDS: DFT; Diacetamide; Dimerization; FT-IR; Relative equilibrium concentrations; Rotamerization

DOCUMENT TYPE: Article

SOURCE: Scopus

Patrone, M.a , Mella, M.a b

Sequential growth simulation of (NH₃)_n clusters (n = 2-8) in ultracold superfluid environment

(2011) Chemical Physics Letters, 514 (1-3), pp. 16-20. Cited 3 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-80052940093&partnerID=40&md5=509fd1c57d7e092803a85e11049b0cde>

md5=3550a54404bb8a833cd454fe8b432b04

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School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

ABSTRACT: The growth of ammonia cluster (NH₃)_n (n = 2-8) in He droplets was studied using a polarizable potential assuming ultrafast heat dissipation and preventing the rearrangement of cluster structures. Energies, structures and isomer statistical distributions were obtained showing that a few high energy isomers may form with a probability similar to low energy ones and that ammonia clusters behave differently from (H₂O)_n for n ≥ 5. Guide by our theoretical analysis, we suggest the need for re-interpreting recent experimental IR spectra of (NH₃)_n in He droplets for 5 ≤ n ≤ 8. © 2011 Elsevier B.V. All rights reserved.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a b

Higher order diffusion Monte Carlo propagators for linear rotors as diffusion on a sphere: Development and application to O₂@He_n

(2011) Journal of Chemical Physics, 135 (11), art. no. 114504, . Cited 6 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-80053190659&partnerID=40&md5=ed3b47bb0cb93e29af99895117227a04>

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ABSTRACT: Exploiting the theoretical treatment of particles diffusing on corrugated surfaces and the isomorphism between the particle on a sphere and a linear molecule rotation, a new diffusion kernel is introduced to increase the order of diffusion Monte Carlo (DMC) simulations involving linear rotors. Tests carried out on model systems indicate the superior performances of the new rotational diffusion kernel with respect to the simpler alternatives previously employed. In particular, it is evidenced a second order convergence toward exact results with respect to the time step of dynamical correlation functions, a fact that guarantees an identical order for the diffusion part of the DMC projector. The algorithmic advantages afforded by the latter are discussed, especially with respect to the a posteriori and on the fly extrapolation schemes. As a first application to the new algorithm, the structure and energetics of O₂@He_n (n 1-40) clusters have been studied. This was done to investigate the possible cause of the quenching of the reaction between O₂ and Mg witnessed upon increasing the size of superfluid He droplets used as a solvent. With the simulations on O₂ indicating a strong localization in the cluster core, the behaviour as a function of n is ascribed to the extremely fluxional compartment of Mg@He_n, which dwells far from the droplet center, albeit being solvated, when n is large. © 2011 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Cargnoni, F.a , Mella, M.b c

Solubility of metal atoms in helium droplets: Exploring the effect of the well depth using the coinage metals Cu and Ag

(2011) Journal of Physical Chemistry A, 115 (25), pp. 7141-7152. Cited 11 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-79959551820&partnerID=40&md5=11b60a0f8ba059019b7b4b8bfcd8038e>

AFFILIATIONS: CNR, ISTM, via Golgi 19, 20133 Milano (I), Italy;
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ABSTRACT: We report a theoretical investigation of the solution properties of Cu and Ag atoms dissolved in He clusters. Employing our recent ab initio ground state pair potential for Me-He (Me = Ag, Cu), we simulated the species Me@He_n (n = 2-100) by means of diffusion Monte Carlo (DMC) obtaining exact information

on their energetics and the structural properties. In particular, we investigated the sensitivity of structural details on the well depth of the two interaction potentials. Whereas Ag structures the first He solvation layer similarly, to some extent, to a positive ion such as Na⁺, Cu appears to require the onset of a second solvation shell for a similar dense structure to be formed despite an interaction well of 28.4 μhartree. An additional signature of the different solution behavior between Ag and Cu appears also in the dependence of the energy required to evaporate a single He atom on the size of the MeHe_n clusters. The absorption spectrum for the 2P ← 2S excitation of the metals was also simulated employing the semi-classical Lax approximation to further characterize MeHe_n (n = 2-100) using novel accurate interaction potentials between He and the lowest 2P state of Ag and Cu in conjunction with the Diatomic-in-Molecules approach. The results indicated that Ag exciplexes should not form via a direct vertical excitation into an attractive region of the excited manifolds and that there is an interesting dependence of the shape of the Cu excitation bands on the local structure of the first solvation shell. © 2011 American Chemical Society.

DOCUMENT TYPE: Article

SOURCE: Scopus

Curotto, E.a , Mella, M.b c

Quantum Monte Carlo simulations of selected ammonia clusters (n=2-5): Isotope effects on the ground state of typical hydrogen bonded systems

(2010) Journal of Chemical Physics, 133 (21), art. no. 214301, . Cited 9 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-79251471772&partnerID=40&md5=f0210b8a40a2dc669a9637d8df25eeb5>

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University Degli Studi Dell Insubria, Via Giuseppe Garibaldi 61, 22100 Como, Italy

ABSTRACT: Variational Monte Carlo, diffusion Monte Carlo, and stereographic projection path integral simulations are performed on eight selected species from the (NH₃)_n, (ND₃)_n, (NH₂D)_n, and (NH₃)_{n-1}(ND₃) clusters. Each monomer is treated as a rigid body with the rotation spaces mapped by the stereographic projection coordinates. We compare the energy obtained from path integral simulations at several low temperatures with those obtained by diffusion Monte Carlo, for two dimers, and we find that at 4 K, the fully deuterated dimer energy is in excellent agreement with the ground state energy of the same. The ground state wavefunction for the (NH₃)₂₋₅ clusters is predominantly localized in the global minimum of the potential energy. In all simulations of mixed isotopic substitutions, we find that the heavier isotope is almost exclusively the participant in the hydrogen bond. © 2010 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a b , Izzo, L.c

Structural properties of hydrophilic polymeric chains bearing covalently-linked hydrophobic substituents: Exploring the effects of chain length, fractional loading and hydrophobic interaction strength with coarse grained potentials and Monte Carlo simulations

(2010) Polymer, 51 (15), pp. 3582-3589. Cited 2 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-77954174223&partnerID=40&md5=fa76c2c7d41ffb956ebb7d91db403986>

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ABSTRACT: Chemical and physical properties of polymeric species in solution strongly depend on their structure, which can be modulated by covalently linking substituents of different solubility. In this work, the effect of changing the

interaction strength and fractional loading of hydrophobic substituents on semi-flexible hydrophilic polymers of varying chain length is studied by means of Monte Carlo simulations and coarse grained model potentials. The latter are chosen in order to provide a more factual representation of a chain in diluted solution, introducing substituent flexibility and realistic torsional and bending potentials. Upon increasing the number and the interaction strength of the substituents, our results indicate a less steep rise of the chain gyration radius and "end to end" distance for the chain length than predicted for an unsubstituted polymer in an almost good solvent. Moreover, a "disordered to compact" structural transition appears. In parallel, the formation of hydrophobic nuclei and the consequent appearance of flexible polymer loops grafted to the semi-rigid cores is witnessed. The core formation resembles a nucleation phenomenon, where the change in the interaction between the substituents modulates the free energy surface for the aggregation process similarly to the change in chemical potential. Interestingly, it has been found that a single chain containing a sufficiently high number of interacting substituents may give rise to the formation of multiple cores, suggesting that the chain stiffness may play a role in defining the structure of the free energy minimum. © 2010 Elsevier Ltd.

AUTHOR KEYWORDS: Hydrophobic substituents; Monte Carlo simulations; Polymers

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M., Harris, K.D.M.

Pathways for hydrogen bond switching in a tetrameric methanol cluster (2009) Physical Chemistry Chemical Physics, 11 (47), pp. 11340-11346. Cited 3 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-73149085503&partnerID=40&md5=6e9d1e1c5ecd15f043c87088c80c5f6>

AFFILIATIONS: School of Chemistry, Cardiff University, Park Place, Cardiff, CF10 3AT, United Kingdom

ABSTRACT: Computational techniques (second order Møller-Plesset MP2 perturbation theory in conjunction with medium and large size basis sets) are applied to explore structural aspects of a hydrogen-bonded tetrameric cluster of methanol molecules, based geometrically on a tetrahedral arrangement of the four oxygen atoms of the cluster. The hydrogen-bonded structures that represent minima on the potential energy surface are established, and the complete set of pathways that allow interconversion between these structures through "switching" of the hydrogen bonding arrangement are elucidated. The implications of these results in terms of dynamic properties of the cluster are discussed. © 2009 The Owner Societies.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.

Effect of the cluster angular momentum J and the projectile orbital momentum L on capture probability and postcollision dynamics

(2009) Journal of Chemical Physics, 131 (12), art. no. 124309, . Cited 1 time.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-70349619769&partnerID=40&md5=117234fb22810f19c9fff3777bcb2652>

AFFILIATIONS: School of Chemistry, Cardiff University, Cardiff CF10 3AT, United Kingdom

ABSTRACT: In this work, collisions between rotating atomic clusters composed of Lennard-Jones (LJn) particles and an identical projectile have been investigated by means of trajectory simulations as a function of the cluster angular momentum J and internal energy E , and for different values of the projectile impact parameter b and relative velocity v_p . As expected, the collision ($P_c(b)$) and capture [or sticking $P_s(b)$] probabilities are found to decay below unity for values of b larger than the average surface radius of the cluster, with dP/db being strongly dependent on v_p . Both $P_c(b)$ and $P_s(b)$, however, appear to be largely insensitive to the modulus of the cluster angular momentum J and only weakly dependent on E for collisions involving target clusters with a lifetime $\tau > 100$ ps. The latter findings are interpreted as indicating the absence of strong changes in the structure of the target as a function of J and E . The

comparison between the dissociation lifetime (τ_{dyn}) of the postcapture complexes ($\text{LJ } n+1^*$) obtained continuing trajectories after monomer capture and the one computed from the fragmentation of statistically prepared clusters (τ_{stat}) supports the validity of a two-step capture-dissociation model; similarly, the comparison between the average amount of energy exchanged during trajectories (ΔE_{dyn}) in the process $\text{LJ } n + \text{LJ} \rightarrow \text{LJ } n+1^* \rightarrow \text{LJ } n + \text{LJ}$ and the one predicted by statistical simulations (ΔE_{stat}) suggests a fast statistical energy redistribution in the collisional complex even for very short τ_{dyn} (e.g., 40 ps). In the case of projectiles aimed at the edge of the cluster [(grazing collisions, $P_c(b) \ll 1$]; however, the time elapsed between formal collision and dissociation, τ_{coll} , is such that $\tau_{\text{coll}} \ll \tau_{\text{stat}}$ and the trajectories indicate the presence of ballistic dynamics and of a weak energy exchange ($\Delta E_{\text{coll}} \ll \Delta E_{\text{dyn}}$, with ΔE_{coll} being the average energy exchanged during collisions). The relevance of these results to the study of gas phase nucleation and to the possibility of building a fully microcanonical framework for its description is discussed. © 2009 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Lubombo, C.a , Curotto, E.a , Janeiro Barral, P.E.b , Mella, M.b
Thermodynamic properties of ammonia clusters (NH_3)_n n=2-11: Comparing classical and quantum simulation results for hydrogen bonded species
(2009) Journal of Chemical Physics, 131 (3), art. no. 034312, . Cited 9 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-67651162239&partnerID=40&md5=daf4b5835e0c13d1dbd7059ec0aeb791>

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ABSTRACT: Classical and quantum simulations of ammonia clusters in the dimer through the hendecamer range are performed using the stereographic projection path integral. Employing the most recent polarizable potential to describe intermolecular interactions, energetic and structural data obtained with our simulations provide support for a more fluxional or flexible nature at low temperature of the ammonia dimer, pentamer, and hexamer than in the other investigated species. The octamer and the hendecamer display a relatively strong melting peak in the classical heat capacity and a less intense but significant melting peak in the quantum heat capacity. The latter are shifted to lower temperature (roughly 15 and 40 K lower, respectively) by the quantum effects. The features present in both classical and quantum constant volume heat capacity are interpreted as an indication of melting even in the octamer case, where a large energy gap is present between its global minimum and second most stable species. We develop a first order finite difference algorithm to integrate the geodesic equations in the inertia ellipsoid generated by n rigid nonlinear bodies mapped with stereographic projections. We use the technique to optimize configurations and to explore the potential surface of the hendecamer. © 2009 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Pappalardo, D.a , Pellicchia, C.b , Milano, G.b , Mella, M.c
Reactivity of a cationic alkyl amino-functionalized cyclopentadienyl aluminum compound with olefins: NMR observation and computational investigation of the single propene insertion product into an Al-C bond
(2009) Organometallics, 28 (8), pp. 2554-2562. Cited 7 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-65749097286&partnerID=40&md5=62118f93dbb224cb3a52a62a7ece4230>

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Dipartimento di Chimica, Università di Salerno, Via Ponte don Melillo, 1-84084, Fisciano (SA), Italy;

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ABSTRACT: In this study the reactivity of the compound dimethyl [2-(N,N-

dmiemylethylen)cyclopentadienyl)Al(III) toward ionizing species and the subsequent reactivity toward ethylene and propene have been explored. Reactions were studied via NMR tube experiments. Upon methyl abstraction by the Lewis acid B(C₆F₅)₃, the amine donor on the ligand side arm coordinates to aluminum, stabilizing the resulting cationic species versus secondary reactions. The obtained cationic species was able to polymerize ethylene, albeit with low activity. Reaction with propene resulted in the selective 1,2-insertion of one propene molecule into an Al-C bond of the Al-Cp moiety. Density functional and ab initio calculations were used to characterize the energy landscape of the insertion into the Al-Cp bond for both ethylene and propene. The computational results suggest this reaction to be more facile than the insertion into the Al-Me bond. © 2009 American Chemical Society.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.

On possible simplifications in the theoretical description of gas phase atomic cluster dissociation

(2009) Journal of Chemical Physics, 130 (8), art. no. 084108, . Cited 3 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-61449085721&partnerID=40&md5=a53fabfae9f9963cec6cbbba34b5d1edf>

AFFILIATIONS: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

ABSTRACT: In this work, we investigate the possibility of describing gas phase atomic cluster dissociation by means of variational transition state theory (vTST) in the microcanonical ensemble. A particular emphasis is placed on benchmarking the accuracy of vTST in predicting the dissociation rate and kinetic energy release of a fragmentation event as a function of the cluster size and internal energy. The results for three Lennard-Jones clusters (LJ_n, n=8,14,19) indicate that variational transition state theory is capable of providing results of accuracy comparable to molecular dynamics simulations at a reduced computational cost. Possible simplifications of the master equation formalism used to model a dissociation cascade are also suggested starting from molecular dynamics results. In particular, it is found that the dissociation rate is only weakly dependent on the cluster total angular momentum J for the three cluster sizes considered. This would allow one to partially neglect the J-dependency of the kinetic coefficients, leading to a substantial decrease in the computational effort needed for the complete description of the cascade process. The impact of this investigation on the modeling of the nucleation process is discussed. © 2009 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Cargnoni, F.a , Kuś, T.b , Mella, M.c , Bartlett, R.J.b

Ground state potential energy surfaces and bound states of M-He dimers

(M=Cu,Ag,Au): A theoretical investigation

(2008) Journal of Chemical Physics, 129 (20), art. no. 204307, . Cited 23 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-57149130608&partnerID=40&md5=931ad302de5946d67fd76c9bde3af79d>

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University of Florida, P.O. Box 118435, Gainesville, FL 32611-8435, United States;

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ABSTRACT: We present an ab initio investigation on the ground state interaction potentials [potential energy surface (PES)] between helium and the group 11 metal atoms: copper, silver, and gold. To the best of our knowledge, there are no previous theoretical PESs proposed for Cu-He and Au-He, and a single one for Ag-He [Z. J. Jakubek and M. Takami, Chem. Phys. Lett. 265, 653 (1997)], computed about 10 years ago at MP2 level and significantly improved by our study. To reach a high degree of accuracy in the determination of the three M-He potentials (M=Cu,Ag,Au), we performed extensive series of test computations to establish the appropriate basis set, the theoretical method, and the computational scheme for these systems. For each M-He dimer we computed the PES

at the CCSD(T) level of theory, starting from the reference unrestricted Hartree-Fock wave function. We described the inner shells with relativistic small core pseudopotentials, and we adopted high quality basis sets for the valence electrons. We also performed CCSDT computations in a limited set of M-He internuclear distances, adopting a medium-sized basis set, such as to define for each dimer a CCSD(T) to CCSDT correction term and to improve further the quality of the CCSD(T) interaction potentials. The Cu-He complex has minimum interaction energy (E_{min}) of $-28.4 \mu\text{hartree}$ at the internuclear distance of 4.59 \AA (R_{min}), and the short-range repulsive wall starts at 4.04 \AA ($RE=0$). Quite interestingly, the PES of Ag-He is more attractive ($E_{\text{min}} = -33.8 \mu\text{hartree}$) but presents nearly the same R_{min} and $RE=0$ values, 4.60 and 4.04 \AA , respectively. The interaction potential for Au-He is markedly deeper and shifted at shorter distances as compared to the lighter complexes, with $E_{\text{min}} = -69.6 \mu\text{hartree}$, $R_{\text{min}} = 4.09 \text{ \AA}$ and $RE=0 = 3.60 \text{ \AA}$. As a first insight in the structure of M-He aggregates, we determined the rovibrational structure of the three M-He dimers. The Cu-He and Ag-He potentials support just few rotational excitations, while the Au-He PES admits also a bound vibrational excitation. © 2008 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Håkansson, P. a b , Mella, M. a

Efficient and robust quantum Monte Carlo estimate of the total and spin electron densities at nuclei

(2008) Journal of Chemical Physics, 129 (12), art. no. 124101, . Cited 3 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-52949104008&partnerID=40&md5=7c38699a4ab012a0c1c8da0fb323b409>

AFFILIATIONS: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom;

Computational Engineering and Design Group, School of Engineering Sciences, University of Southampton, University Road, Southampton SO17 1BJ, United Kingdom

ABSTRACT: The computational performance of two different variational quantum Monte Carlo estimators for both the electron and spin densities on top of nuclei are tested on a set of atomic systems containing also third-row species.

Complications due to an unbounded variance present for both estimators are circumvented using appropriate sampling strategies. Our extension of a recently proposed estimator [Phys. Rev. A 69, 022701 (2004)] to deal with heavy fermionic systems appears to provide improved computational efficiency, at least an order of magnitude, with respect to alternative literature approaches for our test set. Given the importance of an adequate sampling of the core region in computing the electron density at a nucleus, a further reduction in the overall simulation cost is obtained by employing accelerated sampling algorithms. © 2008 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.

Discretization error-free estimate of low temperature statistical dissociation rates in gas phase: Applications to Lennard-Jones clusters $X_{13-n}Y_n$ ($n=0-3$)

(2008) Journal of Chemical Physics, 128 (24), art. no. 244515, . Cited 1 time.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-46149115187&partnerID=40&md5=1f96e1ed57f599501762e096604bdcef>

AFFILIATIONS: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

ABSTRACT: In this work, an improved approach for computing cluster dissociation rates using Monte Carlo (MC) simulations is proposed and a discussion is provided on its applicability as a function of environmental variables (e.g., temperature). With an analytical transformation of the integrals required to compute variational transition state theory (vTST) dissociation rates, MC estimates of the expectation value for the Dirac delta $\delta(q_{\text{rc}} - q_{\text{c}})$ have been made free of the discretization error that is present when a prelimit form for δ is used. As a by-product of this transformation, the statistical error associated with $\langle \delta(q_{\text{rc}} - q_{\text{c}}) \rangle$ is reduced making this step in the calculation of vTST rates substantially more efficient (by a factor of 4-2500, roughly). The improved MC procedure is subsequently employed to compute the

dissociation rate for Lennard-Jones clusters $X_{13-n}Y_n$ ($n=0-3$) as a function of temperature (T), composition, and X-Y interaction strength. The $X_{13-n}Y_n$ family has been previously studied as prototypical set of systems for which it may be possible to select and stabilize structures different from the icosahedral global minimum of X_{13} . It was found that both the dissociation rate and the dissociation mechanism, as suggested by the statistical simulations, present a marked dependence on n , T , and the nature of Y . In particular, it was found that a vacancy is preferentially formed close to a surface impurity when the X-Y interaction is weaker than the X-X one whatever the temperature. Differently, the mechanism was found to depend on T for stronger X-Y interactions, with vacancies being formed opposite to surface impurities at higher temperature. These behaviors are a reflex of the important role played by the surface fluctuations in defining the properties of clusters. © 2008 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Luan, T.a , Curotto, E.a , Mella, M.b

Importance sampling for quantum Monte Carlo in manifolds: Addressing the time scale problem in simulations of molecular aggregates
(2008) Journal of Chemical Physics, 128 (16), art. no. 164102, . Cited 8 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-42949121982&partnerID=40&md5=9e3226980f3273f5749e3f891273d212>

AFFILIATIONS: Department of Chemistry and Physics, Arcadia University, Glenside, PA 19038, United States;

School of Chemistry, Cardiff University, Cardiff CF10 3AT, United Kingdom

ABSTRACT: Several importance sampling strategies are developed and tested for stereographic projection diffusion Monte Carlo in manifolds. We test a family of one parameter trial wavefunctions for variational Monte Carlo in stereographically projected manifolds which can be used to produce importance sampling. We use the double well potential in one dimensional Euclidean space to study systematically sampling issues for diffusion Monte Carlo. We find that diffusion Monte Carlo with importance sampling in manifolds is orders of magnitude more efficient compared to unguided diffusion Monte Carlo. Additionally, diffusion Monte Carlo with importance sampling in manifolds can overcome problems with nonconfining potentials and can suppress quasi-ergodicity effectively. We obtain the ground state energy and the wavefunction for the Stokmayer trimer. © 2008 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Janeiro-Barral, P.E.b , Mella, M.a , Curotto, E.b

Structure and energetics of ammonia clusters $(NH_3)_n$ ($n = 3-20$) investigated using a rigid-polarizable model derived from ab initio calculations
(2008) Journal of Physical Chemistry A, 112 (13), pp. 2888-2898. Cited 14 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-47149105048&partnerID=40&md5=d42eaec0b8efa5394910931f72b6ffb7>

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ABSTRACT: An analytical model has been developed to describe the interaction between rigid ammonia molecules including the explicit description of induction. The parameters of the model potential were chosen by fitting high quality ab initio data obtained using second-order Møller-Plesset (MP2) perturbation theory and extended basis sets. The description of polarization effects is introduced by using a noniterative form of the "charge on spring model", the latter accounting for more than 95% of the dipole induction energy and of the increased molecular dipole. Putative global minima for $(NH_3)_n$ ($n = 3-20$) have been optimized using this new model, the structure and energetics of the clusters with $n = 3-5$ being found in good agreement with previous ab initio results including electronic correlation. Results for larger species have been compared with previous structural studies where only nonpolarizable models were employed. Our model predicts larger binding energies for any cluster size than previous

analytical surfaces, the results often suggesting a reorganization of the relative energy ranking and a different structure for the global minimum. © 2008 American Chemical Society.

DOCUMENT TYPE: Article

SOURCE: Scopus

Lee, M.W.a , Mella, M.b , Rappe, A.M.a

Electronic quantum Monte Carlo calculations of energies and atomic forces for diatomic and polyatomic molecules

(2007) ACS Symposium Series, 953, pp. 69-79.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-36749040369&partnerID=40&md5=ab56d5ca25f27f6b90aba2c5a2d73231>

AFFILIATIONS: Makineni Theoretical Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, United States; School of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, United Kingdom

ABSTRACT: We calculated the energies and atomic forces of first-row monohydrides, carbon monoxide, and small organic polyatomic molecules using quantum Monte Carlo (QMC) method. Accurate forces were obtained with the method of Casalegno, Mella, and Rappe, combining the Hellmann-Feynman theorem forces calculated by the Assaraf-Caffarel method with a many-body Pulay correction. Improved algorithms for the minimization of the variational integral were useful in the force calculations. © 2007 American Chemical Society.

DOCUMENT TYPE: Conference Paper

SOURCE: Scopus

Mella, M.

Macroscopic evidences for non-Rice-Ramsperger-Kassel effects in the reaction between H₃O⁺ and D₂O: The occurrence of nonstatistical isotopic branching ratio (2007) Journal of Chemical Physics, 126 (20), art. no. 204305, .

<http://www.scopus.com/inward/record.url?eid=2-s2.0-34249908335&partnerID=40&md5=d0baf31a36bfb117dbce7e0e60216dd7>

AFFILIATIONS: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

ABSTRACT: The dynamics of the isotopic scrambling in the energized and metastable complex D₂O- H₃O⁺ has been studied using classical molecular dynamics (MD) trajectories starting from regions of phase space corresponding to an already formed collisional complex. The simulations cover the range of internal energies spanned by gas phase collision experiments. Rate constants for the isotopic exchange and the complex dissociation have been computed; the isotopic branching ratio $R = [H D_2 O^+] / [H_2 D O^+]$ has also been obtained from MD simulations and found to deviate substantially from an equivalent prediction based on a previously proposed kinetic scheme. This finding suggests the possibility that details of the reaction dynamics play a role in defining the isotopic branching ratio. The analysis of trajectory results indicated a relatively long lifetime for the collisional complex and the presence of multiple time scales for the exchange process, with a large fraction of the exchange events being separated only by a single oxygen-oxygen vibration or half of it. The occurrence of these fast consecutive jumps and their different probabilities as a function of the relative direction between first and second jumps suggest the presence of ballistic motion in the complex following each reactive event. This can be explained on the basis of overlapping regions in phase space and it is used to provide an explanation of the difference between kinetic and MD branching ratios. © 2007 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Cargnoni, F.a , Mella, M.b , Raimondi, M.c

Application of valence-bond techniques to the study of weakly bound complexes. The potential energy surface of the Ne-CH₄ system

(2007) Physical Chemistry Chemical Physics, 9 (20), pp. 2457-2469. Cited 1 time.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-34248639315&partnerID=40&md5=1d4dc351ae2db95f9fd0743429c6e9fe>

AFFILIATIONS: ISTM-CNR, Via Golgi 19, 20133 Milano, Italy;

School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, United Kingdom;

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ABSTRACT: We present a comprehensive survey of the Molecular Orbital-Valence Bond (MO-VB) method, a theoretical scheme developed within the framework of the Valence Bond theory to deal with weakly bound intermolecular complexes. According to the MO-VB, the wavefunction of the system is expressed as a truncated non-orthogonal Configuration Interaction expansion, which is size extensive and a priori free of basis set superposition error. We report on the recent developments of the method, which extend the range of application of the MO-VB to intermolecular complexes with a quite large number of correlated electrons, showing that VB-based methods are nowadays a valid alternative to Molecular Orbital approaches also in this field. The MO-VB has been applied to study extensively the Ne-CH₄ complex, and compared with the more standard MP4 and CCSD(T) results. We determined two analytical Potential Energy Surfaces (PES) for this system, computed at MO-VB and MP4 level, which represent the first ones coming entirely from ab initio computations. The features of our potentials are discussed, and compared to the single analytical potential which includes the anisotropy available in the literature, determined about twenty years ago by Udo Buck and co-workers using a semiempirical approach [U. Buck, A. Kolhase, D. Secrest, T. Phillips, G. Scoles and F. Grein, *Mol. Phys.*, 1985, 55, 1233]. The differences among the three PES are quite relevant, and are due to play a relevant role in the theoretical simulations of the dynamical properties of the Ne-CH₄ system. © the Owner Societies.

DOCUMENT TYPE: Article

SOURCE: Scopus

Hkansson, P., Mella, M.

Improved diffusion Monte Carlo for bosonic systems using time-step extrapolation "on the fly"

(2007) *Journal of Chemical Physics*, 126 (10), art. no. 104106, . Cited 9 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-33947309567&partnerID=40&md5=e7815ee759c3999ed07ea92508d26f12>

AFFILIATIONS: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

ABSTRACT: A diffusion Monte Carlo algorithm employing "on the fly" extrapolation with respect to the time step is implemented and demonstrated simulating realistic systems. Significant advantages are obtained when using on the fly extrapolation, leading to reduced systematic and statistical errors. The sound theoretical basis of extrapolation on the fly is discussed and compared to justifications for the a posteriori extrapolation. © 2007 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Håkansson, P.a , Mella, M.a , Bressanini, D.b , Morosi, G.b , Patrone, M.b

Improved diffusion Monte Carlo propagators for bosonic systems using Itô calculus (2006) *Journal of Chemical Physics*, 125 (18), art. no. 184106, . Cited 11 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-33750991307&partnerID=40&md5=31fb3361256310fdb4b7be353117fcb8>

AFFILIATIONS: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom;

Dipartimento di Scienze Chimiche ed Ambientali, Università' dell'Insubria, Sede di Como, via Lucini 3, 22100 Como, Italy

ABSTRACT: The construction of importance sampled diffusion Monte Carlo (DMC) schemes accurate to second order in the time step is discussed. A central aspect in obtaining efficient second order schemes is the numerical solution of the stochastic differential equation (SDE) associated with the Fokker-Plank equation responsible for the importance sampling procedure. In this work, stochastic predictor-corrector schemes solving the SDE and consistent with Itô calculus are used in DMC simulations of helium clusters. These schemes are numerically compared with alternative algorithms obtained by splitting the Fokker-Plank operator, an approach that we analyze using the analytical tools provided by Itô calculus. The numerical results show that predictor-corrector methods are indeed

accurate to second order in the time step and that they present a smaller time step bias and a better efficiency than second order split-operator derived schemes when computing ensemble averages for bosonic systems. The possible extension of the predictor-corrector methods to higher orders is also discussed.

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DOCUMENT TYPE: Article

SOURCE: Scopus

Janeiro-Barral, P.E., Mella, M.

Study of the structure, energetics, and vibrational properties of small ammonia clusters $(\text{NH}_3)_n$ ($n = 2-5$) using correlated ab initio methods

(2006) Journal of Physical Chemistry A, 110 (39), pp. 11244-11251. Cited 34 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-33750331502&partnerID=40&md5=d2dfa2776c75e340c98b1a467e151db1>

AFFILIATIONS: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, United Kingdom

ABSTRACT: Equilibrium geometries, interaction energies, and harmonic frequencies of $(\text{NH}_3)_n$ isomers ($n = 2-5$) have been computed using correlated calculations (MP2) in conjunction with Dunning's aug-cc-pVXZ ($X = D, T, Q$) basis sets and the Counterpoise procedure. Whenever available, literature values for the binding energy and geometry of dimers and trimers agree well with our data. Low lying isomers for $(\text{NH}_3)_4$ and $(\text{NH}_3)_5$ have been found to have similar binding energies (roughly 16 and 20 kcal/mol for the tetramer and pentamer, respectively), perhaps suggesting the presence of a very smooth energy landscape. Using BSSE corrected forces or freezing the monomer structure to its gas phase geometry have been found to have only a weak impact on the energetic and structural properties of the clusters. The effect of zero-point energy (ZPE) on the relative stability of the clusters has been estimated using harmonic frequencies. The latter also highlighted the presence of vibrational fingerprints for the presence of double acceptor ammonia molecules. Many-body effects for $(\text{NH}_3)_n$ isomers ($n = 2-4$) have been investigated to explore the possibility of building a pairwise interaction model for ammonia. In the frame of the work presented, we have found the 3-body effect to account for 10-15% of the total interaction energy, whereas the 4-body effects may be neglected as first approximation. © 2006 American Chemical Society.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Ponti, A.b

Alternative low-energy mechanisms for isotopic exchange in gas-phase D $2\text{O}-\text{H}+(\text{H}_2\text{O})_n$ reactions

(2006) ChemPhysChem, 7 (4), pp. 894-903. Cited 8 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-33645812336&partnerID=40&md5=3e924e683f2a86dbbffc1cca4bf80ed>

AFFILIATIONS: School of Chemistry, Cardiff University Main Building, Park Place, Cardiff, CF10 3AB, United Kingdom;

Consiglio Nazionale Delle Ricerche, Istituto di Scienze e Tecnologie Molecolari, via Golgi 19, 20133 Milano, Italy

ABSTRACT: Molecular-dynamics (MD) trajectories and high-level ab initio methods have been used to study the low-energy mechanism for $\text{D}_2\text{O}-\text{H}+(\text{H}_2\text{O})_n$ reactions. At low collisional energies, MD simulations show that the collisional complexes are long-lived and undergo fast monomolecular isomerization, converting between different isomers within 50-500 ps. Such processes, primarily involving water-molecule shifts along a water chain, require the surmounting of very-low-energy barriers and present sizable non-Rice-Ramsperger-Kassel-Marcus (RRKM) effects, which are interpreted as a lack of randomization of the internal kinetic energy. Interestingly, the rate of water shifts was found to increase upon increasing the size of the cluster. Based on these findings, we propose to incorporate the following steps into the mechanism for low-energy isotopic scrambling these D $2\text{O}-\text{H}+(\text{H}_2\text{O})_n$ reactions: a) formation of the collisional complex $[\text{H}+(\text{H}_2\text{O})_n \text{D}_2\text{O}]^*$ in a vibro-rotational excited state; b) incorporation of the heavy-water molecule in the cluster core as HD_2O^+ by means of isomerization involving molecular shifts; c) displacement of salvation molecules from the first shell of

HD20+ inducing de-deuteration (shift of a D+ to a neighbor water molecule); d) reorganization of the clusters and/or expulsion of one of the isotopic variants of water (H2O, HDO or D2O) from the periphery of the complex. © 2006 Wiley-VCH Verlag GmbH & Co. KGaA.

AUTHOR KEYWORDS: Cluster compounds; Molecular dynamics; Protonation; Reaction mechanisms; Water chemistry

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.

Efficient calculation of low energy statistical rates for gas phase dissociation using umbrella sampling

(2006) Journal of Chemical Physics, 124 (10), art. no. 104302, . Cited 3 times. <http://www.scopus.com/inward/record.url?eid=2-s2.0-34547139174&partnerID=40&md5=dbbc4fa2dce8f03bbeb6dc10b16266b2>

AFFILIATIONS: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

ABSTRACT: Monte Carlo (MC) simulations can be used to compute microcanonical statistical rates of gas phase dissociation reactions. Unfortunately, the MC approach may suffer from a slow convergence and large statistical errors for energies just above the dissociation threshold. In this work, umbrella sampling is proposed as a device to reduce the statistical error of MC rate constants. The method is tested by computing the classical dissociation rate for the reaction $[H_5 O_2]^+ \rightarrow H_2 O + H_3 O^+$ over the range of internal energy $38 < E \leq 100$ kcal/mol. Comparing with other literature methods, it is found that umbrella sampling reduces the computational effort by up to two orders of magnitude when used in conjunction with a careful choice of sampling distributions. The comparison between MC rate constants and classical Rice-Ramsperger-Kassel harmonic theory shows that anharmonicity plays an important role in the dissociation process of the Zundel cation ($H_5 O_2^+$) at all energies. © 2006 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Calderoni, G.b , Cargnoni, F.c

Predicting atomic dopant solvation in helium clusters: The MgHe_n case
(2005) Journal of Chemical Physics, 123 (5), art. no. 054328, . Cited 25 times. <http://www.scopus.com/inward/record.url?eid=2-s2.0-23944452692&partnerID=40&md5=60afe86bd548fa8a5c452e505e21ebb3>

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Dipartimento di Chimica Fisica ed Elettrochimica, Università degli Studi di Milano, via Golgi 19, 20133 Milano, Italy;

Istituto di Scienze e Tecnologie Molecolari-Consiglio Nazionale delle Ricerche (ISTM-CNR), via Golgi 19, 20133 Milano, Italy

ABSTRACT: We present a quantum Monte Carlo study of the solvation and spectroscopic properties of the Mg-doped helium clusters MgHe_n with n=2-50. Three high-level [MP4, CCSD(T), and CCSDT] MgHe interaction potentials have been used to study the sensitivity of the dopant location on the shape of the pair interaction. Despite the similar MgHe well depth, the pair distribution functions obtained in the diffusion Monte Carlo simulations markedly differ for the three pair potentials, therefore indicating different solubility properties for Mg in He_n. Moreover, we found interesting size effects for the behavior of the Mg impurity. As a sensitive probe of the solvation properties, the Mg excitation spectra have been simulated for various cluster sizes and compared with the available experimental results. The interaction between the excited P1 Mg atom and the He moiety has been approximated using the diatomics-in-molecules method and the two excited Π1 and Σ1 MgHe potentials. The shape of the simulated MgHe₅₀ spectra shows a substantial dependency on the location of the Mg impurity, and hence on the MgHe pair interaction employed. To unravel the dependency of the solvation behavior on the shape of the computed potentials, exact density-functional theory has been adapted to the case of doped He_n and various energy distributions have been computed. The results indicate the shape of the repulsive part of the MgHe potential as an important cause of the

different behaviors. © 2005 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Lee, M.W.a , Mella, M.b , Rappe, A.M.a

Electronic quantum Monte Carlo calculations of atomic forces, vibrations, and anharmonicities

(2005) Journal of Chemical Physics, 122 (24), art. no. 244103, . Cited 19 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-22544474999&partnerID=40&md5=1a504d0af4fdc83fe398044db9d3a797>

AFFILIATIONS: Makineni Theoretical Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, United States; School of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, United Kingdom

ABSTRACT: Atomic forces are calculated for first-row monohydrides and carbon monoxide within electronic quantum Monte Carlo (QMC). Accurate and efficient forces are achieved by using an improved method for moving variational parameters in variational QMC. Newton's method with singular value decomposition (SVD) is combined with steepest-descent (SD) updates along directions rejected by the SVD, after initial SD steps. Dissociation energies in variational and diffusion QMC agree well with the experiment. The atomic forces agree quantitatively with potential-energy surfaces, demonstrating the accuracy of this force procedure. The harmonic vibrational frequencies and anharmonicity constants, derived from the QMC energies and atomic forces, also agree well with the experimental values. © 2005 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a d , Kuo, J.-L.b , Clary, D.C.a , Klein, M.L.c

Nuclear quantum effects on the structure and energetics of (H₂O)₆H⁺

(2005) Physical Chemistry Chemical Physics, 7 (11), pp. 2324-2332. Cited 25 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-20744452757&partnerID=40&md5=a7635348f716f7075d1faa6bced05aa2>

AFFILIATIONS: Physical and Theoretical Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom;

School of Physical and Mathematical Sciences, Nanyang Technological University, 1 Nanyang Walk, 637616 Singapore, Singapore;

Center for Molecular Modeling, Department of Chemistry, University of Pennsylvania, 231 S. 34th Street, Philadelphia, PA 19104-6323, United States;

School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

ABSTRACT: The energetics and structure of the protonated water hexamer (H₂O)₆H⁺ have been examined employing both model potentials and high-level ab initio methods. To select candidate structures for this cluster, Parallel-Tempering and the OSS2 potential were used as devices to complement the set of stationary points previously optimized by Hodges and Wales, Chem. Phys. Lett., 2000, 324, 279. Structures of these local minima were successively re-optimized using OSS3, B3LYP/aug-cc-pVDZ, and MP2/aug-cc-pVDZ, the latter providing a reference to benchmark the performance of the empirical models and B3LYP method. We found that both OSS2 and OSS3 require a re-parameterization to adequately describe the energetics of some isomers. Zero point energy was found to be important in defining the relative stability of the optimized isomers. The effect of the anharmonicity on the vibrational ground state of (H₂O)₆H⁺ was also examined by means of diffusion Monte Carlo (DMC) and the OSS3 potential, and we found that it accounts for a decrease in total energy of roughly 0-4.4 mE_h. This is a significant effect on the energetics considering that many isomers are nearly degenerate. Including the anharmonic corrections computed with DMC, the branched species were found to be the most stable isomers. The height of the barriers separating a cage or cyclic isomer from a branched one was found to vary from 1.5 to 5.8 mE_h. © The Owner Societies 2005.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.

Improved importance sampling distribution for rate constant calculation (2005) *Journal of Chemical Physics*, 122 (20), art. no. 204106, . Cited 3 times. <http://www.scopus.com/inward/record.url?eid=2-s2.0-20844444809&partnerID=40&md5=2a826f03c908e71cb4f0cc386b10aba3>

AFFILIATIONS: School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom

ABSTRACT: An efficient method to compute the thermal rate constant for rare events within the correlation function $C(t)$ approach is presented. This method, which is based on a modification of the sampling function used to evaluate the dynamical correlation function $C(t)$, can be applied to high-dimensional systems having a rough energy landscape without previous knowledge on the transition states location. In this work, the sampling of a Boltzmann-like distribution for the linear momenta with a lower inverse temperature ($B^* = k T^*$) than the correct one ($B = kT$) is proposed as a way to increase the number of reactive trajectories. The mismatch between the B^* and B distributions is then corrected by a reweighting procedure which allows one to obtain the exact correlation function $C(t)$. The efficiency of this scheme in computing the rate of a particle jumping across the barrier of a simple 2D double well potential is improved by a factor 4–25 depending on the relative value of the original B and modified B^* temperatures. When merged with the "puddle potential" method [S. A. Corcelli, J. A. Rohman, and J. C. Tully, *J. Chem. Phys.*, 118, 1085 (2003)], the new importance sampling function improves the efficiency of the correlation function approach by a factor 16–800 with respect to the unbiased sampling. To test the method in a more challenging case, the previous model system was extended by adding six harmonically restrained particles, each one interacting with the diffusing particle. This model introduces both the possibility of energy exchange and a rougher energy landscape. The new sampling function alone is found to produce an improvement in efficiency of, at least, an order of magnitude when compared with the unbiased case; when merged with the puddle potential method, a 400-fold saving in computer time is found. © 2005 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bertini, L.a , Mella, M.b , Bressanini, D.c , Morosi, G.c

Borromean binding in H_2 with Yukawa potential: A nonadiabatic quantum Monte Carlo study

(2004) *Physical Review A - Atomic, Molecular, and Optical Physics*, 69 (4), pp. 042504–1. Cited 17 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-2942564054&partnerID=40&md5=3dc615b8ad0e0475c2ddcfc14deaa8b0>

AFFILIATIONS: Inst. di Sci./Tecnologie Molecolari, Via Camilla Golgi 19, 20133 Milano, Italy;

Central Chemistry Laboratory, Department of Chemistry, University of Oxford, South Park Road, Oxford OX1 3QH, United Kingdom;

Dipartimento di Scienze Chimiche, Università dell'Insubria, via Lucini 3, 22100 Como, Italy

ABSTRACT: The stability range of the two molecular systems $H_2 +$ and H_2 , whose particles interacted through the Yukawa potential, with varying screening parameter λ was investigated using quantum Monte Carlo technique. Variational Monte Carlo (VMC) calculations were carried out using a one-term function as trial wave function, to optimize the parameters of the trial wave functions for each value of λ . H_2 was found to be stabler than $H_2 +$ for larger value of λ . H_2 being the only stable system for $\lambda > 1.375$ bohr⁻¹ was found to be in the borromean state.

DOCUMENT TYPE: Article

SOURCE: Scopus

Chiesa, S.a , Mella, M.b , Morosi, G.c

Quantum Monte Carlo estimators for the positron-electron annihilation rate in bound and low-energy scattering states

(2004) Physical Review A - Atomic, Molecular, and Optical Physics, 69 (2), pp. 227011-227018. Cited 12 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-1942508040&partnerID=40&md5=bdda413acfl30c5b3c742694f1efd412>

AFFILIATIONS: Department of Physics, Univ. of Illinois Urbana-Champaign, Urbana-Champaign, IL 61801, United States;

Central Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QH, United Kingdom;

Dipartimento di Scienze Chimiche, Università dell'Insubria, via Lucini 3, 22100 Como, Italy

ABSTRACT: An exact scheme to evaluate the positron-electron annihilation rate in bound states and in low-energy scattering processes in the stochastic framework of Monte Carlo methods, was presented. The scheme was tested using four small systems for which accurate results computed by other methods were available. The ground state of PsH and Ps^- and the s-wave component for the scattering of a positron off hydrogen and helium, was considered. The scheme which used Monte Carlo algorithm produced close to exact results.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M., Clary, D.C.

Zero temperature quantum properties of small protonated water clusters $(\text{H}_2\text{O})_n\text{H}^+$ ($n = 1-5$)

(2003) Journal of Chemical Physics, 119 (19), pp. 10048-10062. Cited 41 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0344236122&partnerID=40&md5=32fe9d0e8b67741blb8f328102727080>

AFFILIATIONS: Phys. and Theoretical Chem. Lab., Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom

ABSTRACT: The structure and vibrational motion of the protonated water clusters $(\text{H}_2\text{O})_n\text{H}^+$ ($n=1-5$) were studied using the OSS3 interaction potential and the diffusion Monte Carlo (DMC) method. The aim was to simulate their ground state eigenfunctions. An attempt was also made to compute the ground state energy for neutral water clusters using the same potential to obtain reference values for their proton affinity. The resultant data were analyzed in detail.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Anderson, J.B.b

Intermolecular forces and fixed-node diffusion Monte Carlo: A brute force test of accuracies for He_2 and He-LiH

(2003) Journal of Chemical Physics, 119 (16), pp. 8225-8228. Cited 21 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0242509332&partnerID=40&md5=23999fdff4b19bba5d2d3596df931c6f>

AFFILIATIONS: Dipto. Chim. Fis. ed Elettrochimica, Univ. degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy;

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, United States

ABSTRACT: The FN-DMC method was used to compute accurate values for the interaction energies of He-He and He-LiH . As such, the computed values were in excellent agreement with those of prior "state of the art" electronic structure calculations available for such systems. In using the FN-DMC method, the accuracy of prior CCSD(t) calculations for He-LiH was confirmed.

DOCUMENT TYPE: Article

SOURCE: Scopus

Ponti, A.a , Mella, M.b c

Three-Fragment Counterpoise Correction of Potential Energy Curves for Proton-Transfer Reactions

(2003) Journal of Physical Chemistry A, 107 (38), pp. 7589-7596. Cited 13 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0141925282&partnerID=40&md5=de53834372df9c4efcc8db444df9e357>

AFFILIATIONS: Ist. di Sci. e Tecnologie Molecolari, Consiglio Nazionale delle Ricerche, via Golgi 19, 20133 Milano, Italy;

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Milano, Italy;

Central Chemistry Laboratory, Department of Chemistry, University of Oxford,
South Parks Road, OX1 3QH Oxford, United Kingdom

ABSTRACT: We present a thorough study of the effect of basis set choice and of the three-fragment counterpoise correction for the basis set superposition error on the shape of proton-exchange energy surfaces. This has been investigated by employing the correlated MP2 method and basis sets from cc-pVDZ to aug-cc-pVTZ quality. To understand the effect of the correction and the overall accuracy of the different atomic basis sets, and to discover the best-compromise basis set for large surface scans, we computed the shape difference function between corrected and uncorrected results for the HF2 -, H 3O2 -, H5O2 +, N2H5 -, and N2H7 + systems. Our results show this function to strongly depend on the system, although larger corrections are consistently observed when the more basic fragments (NH2 - and OH-) are involved. Suggestions on which basis set could be used for potential energy surface scans are also given.

DOCUMENT TYPE: Article

SOURCE: Scopus

Chiesa, S.a c , Mella, M.a d , Morosi, G.b , Bressanini, D.b

Comparison of different propagators in diffusion Monte Carlo simulations of noble gas clusters

(2003) Journal of Chemical Physics, 119 (11), pp. 5601-5606. Cited 13 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0141921856&partnerID=40&md5=10384978d180b2c605d71ffed274a931>

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Department of Physics, University of Illinois, Urbana-Champaign, IL 61801, United States;

Central Chemistry Laboratory, Department of Chemistry, University of Oxford,
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ABSTRACT: Short-time approximations of the imaginary-time propagator of the Schrödinger equation were compared on small helium and neon clusters. Comparing the simulations of the same length showed that the algorithm permits the use of larger time steps, that led to more accurate statistics than the ones obtained. The results indicated that the fourth order propagator was preferred to compute the energy, confirming theoretical predictions and numerical results on the model system.

DOCUMENT TYPE: Article

SOURCE: Scopus

Casalegno, M.a b c , Mella, M.a c , Rappe, A.M.b

Computing accurate forces in quantum Monte Carlo using Pulay's corrections and energy minimization

(2003) Journal of Chemical Physics, 118 (16), pp. 7193-7201. Cited 30 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0037723895&partnerID=40&md5=769df777319fe2bde285149dd43cc529>

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ABSTRACT: Various approximate estimates of the nuclear forces were proposed and tested in the framework of the QMC methods. From the results on H 2 and LiH it emerges that computing $\langle F \rangle$ HFT+ $\langle F \rangle \psi$ at the VMC level using a ψ_T whose Jastrow factor was optimized by minimizing the energy, can be an accurate and viable approach to obtain forces. As a result, the computed equilibrium distances were in accurate agreement with the experimental ones.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Colombo, M.C.b c , Morosi, G.b

Ground state and excitation dynamics in Ag doped helium clusters

(2002) Journal of Chemical Physics, 117 (21), pp. 9695-9702. Cited 27 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0036905831&partnerID=40&md5=629c5b696dd3048f1b6c287b41dec5a0>

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ABSTRACT: The energies and structure of silver doped helium clusters were investigated by means of the variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) techniques. The locations of the two maxima of the computed spectrum were found in accurate agreement with the experimental ones differing by less than a 1 nm. The partial energetic overlap between the simulated excitation bands indicated that a vibrational relaxation between the two states was possible.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D.a , Morosi, G.a , Bertini, L.b , Mella, M.b

Stability of few-body systems and quantum Monte-Carlo methods

(2002) Few-Body Systems, 31 (2-4), pp. 199-204. Cited 14 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0038897377&partnerID=40&md5=325c886f38ddcc6855efc1b02b7dab93>

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ABSTRACT: Quantum Monte-Carlo methods are well suited to study the stability of few-body systems. Their capabilities are illustrated by studying the critical stability of the hydrogen molecular ion whose nuclei and electron interact through the Yukawa potential, and the stability of small helium clusters.

DOCUMENT TYPE: Article

SOURCE: Scopus

Chiesa, S.a , Mella, M.a , Morosi, G.b

Orthopositronium scattering off H and He

(2002) Physical Review A - Atomic, Molecular, and Optical Physics, 66 (4), pp. 425021-425028. Cited 30 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0036818591&partnerID=40&md5=4e6b7a4bb6ae03d6a923feaefb51e7dd>

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ABSTRACT: The diffusion Monte Carlo method was employed to compute phase shifts and threshold cross sections for the elastic scattering of positronium off light atoms. The main ideas behind the use of quantum Monte Carlo techniques in scattering problems was reviewed. The comparison of the diffusion Monte Carlo scattering length with other estimates allowed to qualitatively and quantitatively assess the degree of approximation involved in other approaches.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Casalegno, M.a , Morosi, G.b

Positron and positronium chemistry by quantum Monte Carlo VI. The ground state of LiPs, NaPs, e+Be, and E+Mg

(2002) Journal of Chemical Physics, 117 (4), pp. 1450-1456. Cited 22 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0037158117&partnerID=40&md5=054580f2d034d85b0f786539debcl8e0>

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ABSTRACT: The ground states of the positronic complexes LiPs, NaPs, e+Be and

e+Mg, and of the parent ordinary-matter systems were simulated by all electron fixed-node diffusion Monte Carlo (DMC) method. The binding energies of the positronium and positron affinities were computed by direct difference between the DMC energy results. In case of LiPs, the results indicated that the substitution of the potential could be used to study open shell Ps-containing systems without optimizing accurate and expensive trial wave functions.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D.a , Morosi, G.a , Mella, M.b

Robust wave function optimization procedures in quantum Monte Carlo methods (2002) Journal of Chemical Physics, 116 (13), pp. 5345-5350. Cited 48 times. <http://www.scopus.com/inward/record.url?eid=2-s2.0-0036536213&partnerID=40&md5=075ae61bcaa39db8a071fcfa0461d98c>

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ABSTRACT: The discrete nature of the energy variance minimization algorithm was examined in quantum Monte Carlo methods. Optimization of a trial wave function was tested for the helium trimer using several algorithms. The minimization of the mean absolute deviation was shown to be more reliable than the variance minimization and was able to generate trial wave functions with better variational energies.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Chiesa, S.a , Morosi, G.b

Annihilation rate in positronic systems by quantum Monte Carlo: e+LiH as test case

(2002) Journal of Chemical Physics, 116 (7), pp. 2852-2862. Cited 16 times. <http://www.scopus.com/inward/record.url?eid=2-s2.0-0037084370&partnerID=40&md5=1e4aa8b09fe7a139b084729d3b689221>

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ABSTRACT: Methods that may be useful to compute the annihilation rate in positronic systems are compared in the framework of the quantum Monte Carlo (QMC) methods. Furthermore, a simple, but a solid and accurate, method based only on the interparticle distribution sampling is presented. Following testing using model systems, the method is used to compute $\delta(r-)$ for e+LiH for several internuclear distances. The results allow to highlight many interesting features of this positronic complex, and to predict that the annihilation probability increases upon increasing the vibrational quantum number v .

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Bressanini, D.b , Morosi, G.b

Variational Monte Carlo calculation of dynamic multipole polarizabilities and van der Waals coefficients of the PsH system

(2001) Physical Review A - Atomic, Molecular, and Optical Physics, 63 (2), pp. 1-4.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-18344367871&partnerID=40&md5=f5f18361fdbd9218d652968da2e405a2>

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ABSTRACT: The first three dynamic multipole polarizabilities for the ground state of hydrogen, helium, hydride ion, and positronium hydride PsH have been computed using the variational Monte Carlo (VMC) method and explicitly correlated wave functions. Results for the static dipole polarizability by means of the diffusion Monte Carlo method and the finite field approach show the VMC

results to be quite accurate. From these dynamic polarizabilities van der Waals dispersion coefficients for the interaction of PsH with ordinary electronic systems can be computed, allowing one to predict the dispersion energy for the interaction between PsH and less exotic atoms and molecules. ©2001 The American Physical Society.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Bressanini, D.b , Morosi, G.b

Stability and production of positron-diatomic molecule complexes

(2001) Journal of Chemical Physics, 114 (24), pp. 10579-10582. Cited 16 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0035933491&partnerID=40&md5=03d73e8da0ef95da43ee78477e1285de>

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ABSTRACT: The stability and production of positron-diatomic molecule complexes with respect to various dissociation channels was studied. Diffusion Monte Carlo simulations were used to compute energies at geometries close to equilibrium for ground states of positron-diatomic molecule complexes. The analysis showed larger equilibrium distances and vibrational wave numbers for molecules due to the addition of positrons. The findings enabled the prediction of equilibrium geometries and vibrational frequencies for such systems.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bertini, L.a , Mella, M.a , Bressanini, D.b , Morosi, G.b

Explicitly correlated trial wavefunctions in quantum Monte Carlo calculations of excited states of Be and Be-

(2001) Journal of Physics B: Atomic, Molecular and Optical Physics, 34 (3), pp. 257-266. Cited 9 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0035248997&partnerID=40&md5=883f3b77c2dc839e9be494ed53bbf649>

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ABSTRACT: We present a new form of explicitly correlated wavefunction whose parameters are mainly linear, to circumvent the problem of the optimization of a large number of nonlinear parameters usually encountered with basis sets of explicitly correlated wavefunctions. With this trial wavefunction we have succeeded in minimizing the energy instead of the variance of the local energy, as is more common in quantum Monte Carlo methods. We have applied this wavefunction to the calculation of the energies of Be 3P (1s22p2) and Be- 4So (1s22p3) by variational and diffusion Monte Carlo methods. The results compare favourably with those obtained by different types of explicitly correlated trial wavefunction already described in the literature. The energies obtained are improved with respect to the best variational ones found in the literature, and within one standard deviation of the estimated non-relativistic limits.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Bressanini, D.b , Morosi, G.b

Variational Monte Carlo calculation of dynamic multipole polarizabilities and van der Waals coefficients of the PsH system

(2001) Physical Review A - Atomic, Molecular, and Optical Physics, 63 (2), pp. 024503-024501. Cited 2 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0035250987&partnerID=40&md5=69f092a6c8ceae3dde412a51a0db19d8>

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ABSTRACT: Variational Monte Carlo (VMC) method and correlated wave functions were employed for the computation of dynamic multipole polarizabilities for the ground state of hydrogen, helium, hydride ion, and positronium hydride (PsH). The computations were made to understand the species' system behavior upon interaction with an external field. The static dipole polarizability results by Monte Carlo method and the finite field approach depicted the accuracy of the VMC results. The van der Waals dispersion coefficients for the interaction between different systems were computed from the dynamic polarizabilities.
DOCUMENT TYPE: Article
SOURCE: Scopus

Mella, M.a , Morosi, G.a , Bressanini, D.b , Elli, S.b
Positron and positronium chemistry by quantum Monte Carlo. V. the ground state potential energy curve of e+LiH
(2000) Journal of Chemical Physics, 113 (15), pp. 6154-6159. Cited 30 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0034297736&partnerID=40&md5=58362b787172a8613c2eea54c3314833>

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ABSTRACT: The potential energy curve of e+LiH has been computed by means of diffusion Monte Carlo using explicitly correlated trial wave functions. This curve allows us to compute the adiabatic total and binding energies and the vibrational spectrum of e+LiH, and the adiabatic positron affinity of LiH. Using these results, we discuss the possibility to detect spectroscopically e+LiH in the gas phase, in order to have the first direct observation of a positron-containing system. © 2000 American Institute of Physics.

DOCUMENT TYPE: Article
SOURCE: Scopus

Mella, M.a , Morosi, G.a , Bressanini, D.b
Response to "Comment on 'Positron and positronium chemistry by quantum Monte Carlo. IV. Can this method accurately compute observables beyond energy?'"
(2000) Journal of Chemical Physics, 112 (8), pp. 3928-3929.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-84883501485&partnerID=40&md5=dce9758c71e40dfffc2683bbd3bc2eac4>

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DOCUMENT TYPE: Letter
SOURCE: Scopus

Mella, M.a , Morosi, G.a , Bressanini, D.b
Time step bias improvement in diffusion Monte Carlo simulations
(2000) Physical Review E - Statistical Physics, Plasmas, Fluids, and Related Interdisciplinary Topics, 61 (2), pp. 2050-2057. Cited 12 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0009104614&partnerID=40&md5=7e60448247875e8fbd91f3477644608>

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Dipto. Sci. Chimiche, Fisiche M., Università dell'Insubria, Polo di Como, via Lucini 3, 22100 Como, Italy

ABSTRACT: A Makri-Miller approximation to the exact propagator and the improved split-operator propagator proposed by Drozdov are implemented within the diffusion Monte Carlo method for the simulation of boson systems, and confronted with the Trotter formula and with the importance sampling technique. As a preliminary approach, we compute analytically the time step bias of the mean energy for the different propagators in the simple case of the harmonic oscillator. These results indicate the improved split-operator propagator as the most accurate. Simulations on one- and three-dimensional model systems confirm the analytical results showing that this propagator is very efficient in reducing the time step bias, therefore improving the efficiency of the algorithm.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Morosi, G.a , Bressanini, D.b

A diffusion Monte Carlo accurate interaction potential between H and PsH (2000) Journal of Chemical Physics, 112 (3), pp. 1063-1065. Cited 11 times. <http://www.scopus.com/inward/record.url?eid=2-s2.0-0001106086&partnerID=40&md5=f50144a526145e6870dc64a7b51e8159>

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ABSTRACT: The interaction potential between H and PsH, and between H and H have been calculated using the diffusion Monte Carlo method. As far as the H-H-system is concerned, our results appear to be the most accurate published so far. The potential functions show the H-PsH system to be bound with respect to the H₂+Ps dissociation channel for nuclear distances larger than 3.5 bohr, while the H-2 - e⁺ threshold lies 0.25 hartree above for all the distances studied. Moreover, the H-PsH potential curve presents a minimum located at 5.2 bohr that can be attributed to the van der Waals interaction between the two fragments. The relevancy of these results for the low energy scattering of Ps on H₂ and for the exchange reaction of H with Ps is discussed. © 2000 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D.a , Zavaglia, M.a , Mella, M.b , Morosi, G.b

Quantum Monte Carlo investigation of small 4He clusters with a 3He impurity (2000) Journal of Chemical Physics, 112 (2), pp. 717-722. Cited 44 times. <http://www.scopus.com/inward/record.url?eid=2-s2.0-0001309756&partnerID=40&md5=dfb9c389f698cbf2ed4e46adcd9f8d3f>

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ABSTRACT: Small helium (4He) clusters containing the lighter isotope 3He are studied by means of quantum Monte Carlo methods. Accurate ground state energies and structural properties are obtained using accurate trial wave functions and the Tang-Tonnesen-Yiu (TTY) helium-helium pair potential. The dimer 4He-3He is not bound; as well as the trimer 4He₃He₂. The smallest cluster containing 3He is 4He₂ 3He with a nonrigid structure having a marked linear contribution. Interestingly, this weakly bound system, with an energy one order of magnitude less than the 4He₃ trimer, is able to bind another 3He atom, forming the tetramer 4He₂ 3He₂, which shows the odd feature of having five out of six unbound pairs. In general, the substitution of a single 4He atom in a pure cluster with a 3He atom leads to an energetic de stabilization, as the pair 4He-3He is not bound. The isotopic impurity is found to perturb only weakly the distributions of the remaining 4He atoms, which retain the high floppiness already found in the pure clusters. As the number of atoms increases the isotopic impurity has the marked tendency to stay on the surface of the cluster. This behavior is consistent with the formation of the so-called "Andreev states" of a single 3He in liquid 4He helium and droplets, where the impurity tends to form single-particle states on the surface of the pure 4He. © 2000 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Casalegno, M.a , Mella, M.a , Morosi, G.a , Bressanini, D.b

Quantum Monte Carlo study of the H- impurity in small helium clusters (2000) Journal of Chemical Physics, 112 (1), pp. 69-76. Cited 18 times. <http://www.scopus.com/inward/record.url?eid=2-s2.0-0002331093&partnerID=40&md5=7763b4ea0d1e0ddeb70191f55a25168b>

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ABSTRACT: We report ground state energies and structural properties for small helium clusters (4He) containing a H- impurity computed by means of variational and diffusion Monte Carlo methods. Except for 4He2H- that has a noticeable contribution from collinear geometries where the H- impurity lies between the two 4He atoms, our results show that 4HeNH- clusters have a compact 4HeN subsystem that binds the H- impurity on its surface. The results for N \geq 3 can be interpreted invoking the different features of the minima of the He-He and He-H- interaction potentials. © 2000 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bertini, L.a , Bressanini, D.b , Mella, M.a , Morosi, G.a

Linear expansions of correlated functions: Variational Monte Carlo case study (1999) International Journal of Quantum Chemistry, 74 (1), pp. 23-33. Cited 6 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0008837563&partnerID=40&md5=f143a996ea5bf30e3d050216146845c6>

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ABSTRACT: The relative performance of trial wave functions expressed as linear combination of correlated exponentials has been tested on a variety of systems. The results are compared against other correlated functions commonly used in the literature to assess the capabilities of the proposed ansatz. A possible departure from the simple exponential functional form used in previous works is discussed, along with its advantages and drawbacks. We also discuss how to implement an efficient optimization procedure for this correlated basis set. © 1999 John Wiley & Sons, Inc.

AUTHOR KEYWORDS: Correlated wave functions; Few-electron systems; Quantum Monte Carlo; Variance optimization; Variational Monte Carlo

DOCUMENT TYPE: Article

SOURCE: Scopus

Morosi, G.a , Mella, M.a , Bressanini, D.b

Quantum Monte Carlo calculations of molecular electron affinities: First-row hydrides

(1999) Journal of Chemical Physics, 111 (15), pp. 6755-6758. Cited 9 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0000697956&partnerID=40&md5=6fb759c79d63afa8c85b6c42a31db801>

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ABSTRACT: Very accurate energies can be computed by the fixed-node diffusion Monte Carlo method. They are affected only by the nodal error due to the approximate description of the nodal surfaces by the trial wave function. We examine the cancellation of nodal errors in molecular electron affinity calculations. Ground state energies of the anions of first-row hydrides AH (A=Li-O) have been computed using the fixed-node diffusion Monte Carlo method with a determinant times a correlation factor as the trial wave function. The energies are among the lowest to date. Using the energy values for the neutral molecules computed by Luchow and Anderson [A. Luchow and J. B. Anderson, J. Chem. Phys. 105, 7573 (1996)] we computed adiabatic electron affinity values and found them in agreement with the experimental data. As a consequence, the values of the anion dissociation energies are also correctly evaluated. © 1999 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D.a , Fabbri, G.a , Mella, M.b , Morosi, G.b

A spline approach to trial wave functions for variational and diffusion Monte

Carlo

(1999) Journal of Chemical Physics, 111 (14), pp. 6230-6237. Cited 2 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0009409162&partnerID=40&md5=ecf72619653737870cd703339656d08a>

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ABSTRACT: We describe how to combine the variational Monte Carlo method with a spline description of the wave function to obtain a powerful and flexible method to optimize electronic and nuclear wave functions. A property of this method is that the optimization is performed "locally": During the optimization, the attention is focused on a region of the wave function at a certain time, with little or no perturbation in far away regions. This allows a fine tuning of the wave function even in cases where there is no experience on how to choose a good functional form and a good basis set. After the optimization, the splines were fitted using more familiar analytical global functions. The flexibility of the method is shown by calculating the electronic wave function for some two and three electron systems, and the nuclear wave function for the helium trimer. For $4\text{He } 3$, using a two-body helium-helium potential, we obtained the best variational function to date, which allows us to estimate the exact energy with a very small variance by a diffusion Monte Carlo simulation. © 1999 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a , Morosi, G.a , Bressanini, D.b

Positron and positronium chemistry by quantum Monte Carlo. IV. Can this method accurately compute observables beyond energy?

(1999) Journal of Chemical Physics, 111 (1), pp. 108-114. Cited 36 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0000225145&partnerID=40&md5=91cbd58ede3c930dbdc5aeab9a76af94>

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ABSTRACT: Many different properties of the positron containing systems PsH , $[\text{Li}, e^+]$, LiPs , and $[\text{LiH}, e^+]$, were computed using both variational Monte Carlo and fixed node diffusion Monte Carlo methods, and explicitly correlated trial wave functions. Our results show that these techniques can accurately compute not only energy values, but also other observables. Our $\langle \delta(r^+) \rangle$ values for PsH , $[\text{Li}, e^+]$, and LiPs are in good agreement with the most recent state of the art correlated calculations, while for $[\text{LiH}, e^+]$ our calculations are the first to give reliable results. © 1999 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D.a , Mella, M.b , Morosi, G.b

Stability of four-body systems in three and two dimensions: A theoretical and quantum Monte Carlo study of biexciton molecules

(1998) Physical Review A - Atomic, Molecular, and Optical Physics, 57 (6), pp. 4956-4959. Cited 8 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-11744346671&partnerID=40&md5=93b0a3a208f6d386f4d31172b0600b87>

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ABSTRACT: The stability of four-body systems $(m_a+m_b+m_1-m_2)$ in three (3D) and two dimensions (2D) is discussed using accurate numerical results obtained by means of diffusion Monte Carlo calculations. In 3D, we extend our proof of the stability for the class of systems $(m_a+m_b+m_1-m_1)$, showing that they are stable against the dissociation in (m_a+m_1) and (m_b+m_1) for any value of the mass ratio m_a/m_b . In 2D, using the ground-state energy of the dipositronium, it is

possible to prove that the stability of four-body systems follows the same scenario. We also give upper and lower bounds to the binding energies for the class (M+M+m-m-in 2D, useful to discuss the relative stability of biexciton molecules in semiconductors.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D.a , Mella, M.b , Morosi, G.b

Positron chemistry by quantum Monte Carlo. II. Ground-state of positron-polar molecule complexes

(1998) Journal of Chemical Physics, 109 (5), pp. 1716-1720. Cited 48 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0001617079&partnerID=40&md5=2b79a1370f6bd3a663affa9e884468b9>

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ABSTRACT: The stability of the ground-state of positron-polar molecule complexes [M,e +] has been explored for M=LiH, HF, H₂O, BeO, LiF using variational and diffusion Monte Carlo techniques. Our simulations show that the ground-state of the complexes [LiH,e +] 2,1Σ⁺, [BeO,e +] 2,1Σ⁺, and [LiF,e +] 2,1Σ⁺ is stable against the dissociation either in the two fragments M and e⁺ or in the other two fragments M⁺ and Ps=[e⁺,e⁻], while the ground-state of [H₂O,e +] 2,1A₁ and of [HF,e +] 2,1Σ⁺ has an energy equal to the dissociation threshold, M and e⁺. We also compare the predicted vertical positron affinity (PA) with high quality vertical electron affinity (EA) and discuss the relevant difference between the two values. © 1998 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D.a , Mella, M.b , Morosi, G.b

Positron and positronium chemistry by quantum Monte Carlo. III. Ground state of [OH,Ps], [CH,Ps], and [NH₂,Ps] complexes

(1998) Journal of Chemical Physics, 109 (14), pp. 5931-5934. Cited 20 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0001349344&partnerID=40&md5=0823ed2f05ad1dd4fd7d5b52cb57cbd6>

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ABSTRACT: The stability of the [OH,Ps], [CH,Ps] and [NH₂,Ps] complexes, where Ps=(e⁺,e⁻), have been studied using Monte Carlo techniques and explicitly correlated trial wave functions. For these systems we have computed the ground state energy values using both variational Monte Carlo and fixed node diffusion Monte Carlo methods. Diffusion Monte Carlo results allow us to predict [OH,Ps] and [CH,Ps] systems to be stable against positron and Positronium (Ps) loss. As far as [NH₂,Ps] is concerned, its small value of the Binding Energy (BE) does not allow us to conclude about its stability: this is discussed qualitatively including zero point motion of the atoms in the complex. © 1998 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D.a , Mella, M.b , Morosi, G.b

Positronium chemistry by quantum Monte Carlo. I. Positronium-first row atom complexes

(1998) Journal of Chemical Physics, 108 (12), pp. 4756-4760. Cited 71 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0000836585&partnerID=40&md5=17510116eac9df8bc02f0141d025ecc6>

AFFILIATIONS: Ist. Sci. Matematiche, Fisiche C., Univ. degli Studi di Milano, Sede di Como, via Lucini 3, 22100 Como, Italy;
Dipto. Chim. Fis. ed Elettrochimica, Univ. degli Studi di Milano, via Golgi 19, 20133 Milano, Italy

ABSTRACT: The stability of the ground and excited states of Positronium-atom

complexes $[A, Ps]$, $Ps = [e^+, e^-]$, has been explored for $A=Li, B, C, O, F$ using variational and diffusion Monte Carlo techniques. From the numerical results of our simulations it turns out that the ground state of the complexes $[Li, Ps]$ 2S, $[C, Ps]$ 3S, $[O, Ps]$ 1P, and $[F, Ps]$ 2S is stable against the break up in the two neutral fragments A and Ps , while the ground state of $[B, Ps]$ 2P has an energy above the same dissociation threshold. As to the excited states, the only possible candidate, $[F, Ps]$ 2P, has a total energy statistically equal to the lower dissociation threshold, i.e. it does not seem to be stable against the dissociation. © 1998 American Institute of Physics.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D.a , Mella, M.b , Morosi, G.b

Stability and positron annihilation of positronium hydride $L=0,1,2$ states: A quantum Monte Carlo study

(1998) Physical Review A - Atomic, Molecular, and Optical Physics, 57 (3), pp. 1678-1685. Cited 29 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0000272096&partnerID=40&md5=4518cf01b4a7f618b1d9b18f4319c990>

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ABSTRACT: States of positronium hydride having different angular momenta have been studied by means of quantum Monte Carlo techniques. Explicitly correlated wave functions for different states have been obtained using the variational Monte Carlo optimization method. These wave functions have been used in variational Monte Carlo and diffusion Monte Carlo (DMC) simulations to compute energies, annihilation rates, and other observables. Our DMC results compare well with the best published variational ground-state binding energy, and show that positronium hydride has metastable states with angular momentum $L=1$ and 2 above the ground-state dissociation threshold. The values of the other observables for the ground state are comparable with the best variational calculations. The results for the $L=1$ and 2 states are used to discuss a proposed model for the annihilation of positrons in alkali hydrides crystals.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D.a , Mella, M.b , Morosi, G.b

Stability of four-unit-charge systems: A quantum Monte Carlo study

(1997) Physical Review A - Atomic, Molecular, and Optical Physics, 55 (1), pp. 200-205. Cited 49 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0000932268&partnerID=40&md5=e0222f8058bf711c97583f3c782e03eb>

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ABSTRACT: The family of four-particle systems $(M^+m^+M^-m^-)$ has been studied by means of Monte Carlo techniques. Nonadiabatic explicitly correlated wave functions for different values of the mass ratio M/m have been obtained using a variational Monte Carlo optimization method. These wave functions have been used in diffusion Monte Carlo simulations of $(M^+m^+M^-m^-)$ to compute exact ground-state energies. Our results enlarge the stability range of the mass ratio for these and for similar less symmetric systems and address the problem of the stability of the hydrogen-antihydrogen system. For the special case of the dipositronium molecule ($M=m$) we report the ground-state energy, consistent with previous accurate calculations, and average values of various observables.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D.a , Mella, M.b , Morosi, G.b

Nonadiabatic wavefunctions as linear expansions of correlated exponentials. A quantum Monte Carlo application to $H^+ 2$ and Ps^2

(1997) Chemical Physics Letters, 272 (5-6), pp. 370-375. Cited 16 times.
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0031552558&partnerID=40&md5=71398756c42434230bbb8101f4a89e3e>

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ABSTRACT: We propose to expand the nonadiabatic solution of the Schrödinger equation as a linear combination of explicitly correlated exponentials. A series of trial wavefunctions has been optimized minimizing the variance of the local energy for the H⁺ 2 and dipositronium (Ps₂) molecules in their ground state, without resorting to the Born-Oppenheimer approximation: the calculations have been performed using the variational Monte Carlo method. In a diffusion Monte Carlo simulation a 6-term wavefunction allowed us to compute the exact energy of the Ps₂ system -0.51601 hartree with a variance of 0.00001 hartree. © 1997 Elsevier Science B.V.

DOCUMENT TYPE: Article

SOURCE: Scopus

Mella, M.a b , Lüchow, A.b , Anderson, J.B.b

An improved transition matrix for variational quantum Monte Carlo

(1997) Chemical Physics Letters, 265 (3-5), pp. 467-472. Cited 9 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0031556981&partnerID=40&md5=fd5607bd50d89a0199a6cb84e6a14ca4>

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Department of Chemistry, Pennsylvania State University, University Park, PA 16802, United States

ABSTRACT: An improved transition matrix for variational Monte Carlo calculations is proposed. This matrix allows the use of larger time steps than the usual Langevin-based transition matrix and provides efficient sampling of electron positions in both the core and valence regions. Its efficiency and accuracy in predictions of energies for hydrogen-like systems and for the neon atom are demonstrated.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bianchi, R., Bressanini, D., Cremaschi, P., Mella, M., Morosi, G.

Wave-function optimization by least-squares fitting of the exact wave function sampled by quantum Monte Carlo

(1996) International Journal of Quantum Chemistry, 57 (3), pp. 321-325. Cited 12 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0008821206&partnerID=40&md5=8387c0e36e093493f885ed2418bc3735>

AFFILIATIONS: Dipto. Chim. Fis. ed Elettrochimica, Ctro. CNR Stud. Relazioni T., Via Golgi 19, 20133 Milan, Italy

ABSTRACT: The sampling of the exact solution of the Schrödinger equation by quantum Monte Carlo methods allows one to solve the problem of the optimization of linear and nonlinear parameters of a trial wave function by minimization of the distance to the exact wave function in Hilbert space even for those systems whose exact wave function is unknown. The overlap integrals between the basis functions and the exact wave function can be easily estimated within the quantum Monte Carlo formalism. Several observables of the helium atom ground state, computed both within the orbital approximation and by an explicitly correlated basis set, evidence the overall goodness of the wave function optimized according to this criterion. © 1996 John Wiley & Sons, Inc.

DOCUMENT TYPE: Article

SOURCE: Scopus

Bressanini, D., Mella, M., Morosi, G.

Many-electron correlated exponential wavefunctions. A quantum Monte Carlo application to H₂ and He₂ +

(1995) Chemical Physics Letters, 240 (5-6), pp. 566-570. Cited 16 times.

<http://www.scopus.com/inward/record.url?eid=2-s2.0-0010794333&partnerID=40&md5=71398756c42434230bbb8101f4a89e3e>

md5=96157868801fe9ff4c9713c1967eb242

AFFILIATIONS: Dipartimento di Chimica Fisica ed Elettrochimica, Universita' di Milano, via Golgi 19, 20133 Milano, Italy

ABSTRACT: We propose to expand the solution of the Schrödinger equation for an atomic or molecular system as a linear combination of many-electron explicitly correlated exponentials. A series of trial wavefunctions has been optimized, minimizing the variance of the local energy for H₂ and He₂ + in their ground state at the equilibrium distance, and their variational energy has been computed using the variational Monte Carlo method. The He₂ + wavefunctions have been used in a series of fixed node diffusion Monte Carlo simulations, showing that, using a small number of terms, one can obtain a good estimate of the exact energy. © 1995.

DOCUMENT TYPE: Article

SOURCE: Scopus