Calculations of the spectral shifts and line profiles of alkaline earth atoms in liquid helium environment

Lucas Modesto-Costa [a], Kaline Coutinho [a], Prasanta K. Mukherjee [b,c], Sylvio Canuto [a,*]

[a] Instituto de Física, Universidade de São Paulo, CP 66318, 05314-970 São Paulo, SP, Brazil
[b] Department of Physics, Ramakrishna Mission Vivekananda University, P.O. Belur Math, Howrah 711202, West Bengal, India
[c] Department of Mathematics, Visva-Bharati University, Santiniketan 731235, West Bengal, India

ARTICLE INFO

ABSTRACT

Liquid configurations generated by Metropolis Monte Carlo simulations are used in time-dependent density functional theory calculations of the spectral line shifts and line profiles of the lowest lying excitation of the alkaline earth atoms, Be, Mg, Ca, Sr and Ba embedded in liquid helium. The results are in very good agreement with the available experimental data. Special attention is given to the calculated spectroscopic shift and the associated line broadening. The analysis specifies the inhomogeneous broadening of the three separate contributions due to the splitting of the $s \rightarrow p$ transition of the alkaline earth atom in the liquid environment.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Spectroscopic properties of foreign atom embedded in liquid helium have been extensively investigated experimentally during the past few decades and the subject has been well reviewed [1]. Such investigations yield not only the spectral properties of the confined atoms but also suggest a possible way of determining the quantum fluid properties using the foreign atoms as sensitive microprobes [2,3]. Modern techniques of facilitating implantation of foreign particles have made experimental investigations possible for a large section of atoms of the periodic table along with such studies for ions and molecules [1,4,5]. The electronic charge cloud of a free atom is subjected to a different potential when embedded under liquid helium environment and experiences a strong Pauli repulsion at the boundary. As a result a cavity is formed, the size of which is determined by the nature of the central atom, its angular momentum and the He-atom pair potential. The diameter of the atomic bubble is typically of the order of 8–12 Å [5–7] but in the case of an electron the bubble diameter is expected to be as large as 34 Å [1]. The outcome of such a confinement is to shift the spectral line positions and alter the spectral line profiles compared to the free atomic system, which are observed in various experiments with optical excitations [1]. The amount of the shift depends on the binding energy of the external electron and the nature of the pair potential between the central atom and helium. In this regard alkali atoms are expected to have comparatively large shifts followed by alkaline earth atoms.

Because of the weak interaction between the foreign atom and the surrounding helium the absolute values of the shifts are small [1]. However, the excitation lines are found to be blue shifted with comparatively larger magnitudes compared to the usually red shifted emission lines [1,8]. Accurate laser spectroscopic data are available for the excitation and emission spectra of the higher lying alkali atoms Rb and Cs along with Na_2 and Li_2 embedded in liquid helium, together with their line profiles, while no such data seem to be available for the lower lying members Li, Na and K [4]. A number of experiments have been performed for the liquid helium embedded alkaline earth atoms Be, Mg, Ca, Sr and Ba for the estimation of line shifts and line profiles [9–16].

On the theoretical side the effort to describe these small spectral shifts in such weakly interacting system is in progress and it is recognized to be a great challenge. Conventional solvation methods using the continuum approximation are of little utility. This is because, in addition to these complicating aspects, both the solute and the solvent are atomic, thus nonpolar, systems. Most of the theoretical studies have then used the standard bubble model [1,4,17–20] which in spite of the relative success in describing spectral line shifts [1,8] has limited value in obtaining line broadening [21–25]. But attempts have been made to estimate theoretically the line shifts in alkali atoms [8,26,27] and in the alkaline earth series Be, Mg, Ca, Sr and Ba [10,28,29]. Symmetry adapted cluster configuration interaction (SAC-CI) method has been applied for the calculation of the excitation line shift of the D line of Na embedded in liquid helium by Saha et al. [30] using a fixed cluster providing reasonably good results. The relativistic density functional estimates of the shifts and widths of the principal resonance lines of Na, Rb and Cs with fixed cluster model by Anton et al.

* Corresponding author. Fax: +55 11 3813 4334.
E-mail address: canuto@if.usp.br (S. Canuto).

[31,32] yield very encouraging results. A recent review of the different methods adopted for interpreting experimental data is available [33].

The first theoretical investigation using statistical consideration and modern quantum chemical methods was due to Ludwig et al. [34] on Na–He system in which the liquid structures around the central atom Na were generated using Monte Carlo (MC) simulation technique. This was followed by a time dependent density functional theory (TDDFT) estimation of the spectral line shift of the Na D line and its width. However, for Na, no direct experimental evidence exists but the results compared favorably with available theoretical data. This sequential Monte Carlo/quantum mechanics (S-MC/QM) methodology [35–37] was also successfully applied by Modesto-Costa et al. [38] for the estimation of line shift and broadening of Na_2 embedded in liquid helium for which accurate laser spectroscopic data are available [4].

In this Letter we present the results of our detailed investigations on the first optically allowed excited state of the alkaline earth atoms Be, Mg, Ca, Sr and Ba embedded in liquid helium based on the S-MC/QM methodology. We report an unified approach where the alkaline earth and He atoms are treated at the same level of methodology. As the liquid structures are obtained from a MC simulation the statistical condition is naturally included. This leads to the possibility of obtaining the inhomogeneous broadening of the absorption band compared to the free atom situation. The results thus include both the line shift and broadening in respective cases which are converged with respect to the statistics and the number of explicit environmental atoms. The line width has three contributions of interest derived from the splitting of the $s \rightarrow p$ transition. As the dominant theoretical approach is still the standard bubble model, or an optimized cluster configuration, we also perform a cluster calculation and contrast the results with those obtained using the liquid configurations. In addition, we compare the cavity obtained from the MC simulation with the expected bubble radius.

Each value of the excitation energy in the liquid helium environment is the result of a statistical average over more than 100 statistically uncorrelated configurations. The use of statistically uncorrelated configuration is very important to ensure a fast statistical convergence [37]. In total, nearly 1500 quantum mechanical calculations are performed to obtain the most systematic theoretical study of the spectroscopic changes of the alkaline earth atoms in liquid helium environment.

2. Methodology

We consider the alkaline earth atoms Be, Mg, Ca, Sr and Ba under liquid helium and we designate them as R. The liquid helium structures around all the different systems R–He have been generated by MC simulation using Metropolis sampling technique [39] with Lennard–Jones pair potential in the standard NPT ensemble. The structures are generated using a pair potential for the R–He and He–He systems. For the R–He interaction we adopted the CCSD(T) potentials due to Lovallo and Klobukowski (LK) [40] calculated using well tempered model core potentials. The parameters for the potentials appear to be very consistent for the systems under study. For Ca–He we have additionally used the potential due to Czuchaj et al. (CRSP) [41] calculated using pseudopotential technique based on experimental parameters and for Be–He system we also used the CCSD potential due to LK [40]. The He–He potential has been consistently used in previous calculations [34,38]. In the MC simulation we used 1 R atom with 999 He atoms. The temperature is fixed at 3 K, slightly above the critical temperature. It was experimentally shown that the spectral properties are unaffected by changes above or below the critical temperature [13]. The sampling of the configurations is made in each case after

obtaining the auto correlation function of energy [42,43]. The contribution from the He atoms within the first solvation shell in respective cases with the chosen pair potential has been explicitly taken into account in the subsequent all electron QM calculations.

For the QM calculation of the excitation spectra of the R–He system we adopted the TDDFT in which we have mainly used the exchange correlation functionals O3LYP, due to Handy and Cohen [44], and PBE1PBE due to Perdew et al. [45] as we have found from previous experience [34,38] these functional to yield consistent results. The inaccuracy of the present DFT methods to describe the known multiconfiguration ground state of Be makes this questionable. However, our interest lies in the spectral shift and thus Be is also considered for the sake of completeness. For the He atom we have mainly used the known triple zeta with diffuse and polarized functions *6-311++G(2d,2p)* basis set while for the atom R we used the quadruple zeta valence quality *def2-qzvp* basis set due Weigend and Ahlrich [46]. For Sr and Ba atoms, the *def2-qzvp* uses effective core potential [47]. For Ba–He we have probed the role of other basis sets for He as well as for Ba, but consistent results are obtained with the two sets mentioned above. The present calculations are non-relativistic, but relativistic effects seem to be small [31,32]. In the experiments the initial ^1S state is excited to a ^1P state having only one level ($S = 0$, $L = 1$) with $J = 1$ and thus having no possibility of spin-orbit splitting. In the experimental observations only one line with inhomogeneous broadening is observed.

The MC simulations and the necessary quantum mechanics interface were done using the Dice program [48] and the quantum mechanical calculations have been performed using GAUSSIAN 09 program [49].

3. Results and discussion

First we consider the structural coordination of the helium atoms around the foreign alkaline earth atom. Figure 1 shows the radial distribution functions between R and the He atom using the interatomic potential of LK [40] for the cases Be, Mg, Ca, Sr and Ba. For the Ca–He system we have additionally used the potential of Czuchaj et al. [41], and it is named Ca* in Figure 1. The figure shows that the solvation shells become broader with increasing of the atomic number of the central atom and with a gradual shift of the peak position towards larger distance. The changes in the spectral properties are mainly due to the interatomic interaction coming from the first solvation shell due to a rapid decrease of this interaction with the distance. The first solvation shell obtained with the LK potential for the Be–He system has a maximum at 4.4 Å starting at 4.0 Å and ending at 5.9 Å. This includes 26 neighboring He atoms in the first solvation shell. With the LK CCSD potential we get the same number of nearest neighbors with very similar distribution. TDDFT calculations have been performed in this supersystem of 26 He atoms surrounding the central Be atom with the basis sets mentioned before. The transition energy of the $2s \rightarrow 2p$ excitation line for the free and liquid He embedded Be atom has been calculated with each basis set. The result of the calculated shifts and widths are displayed in Table 1. There is no experimental result for the spectral shift of the absorption spectrum of Be in liquid helium. Some indirect evidence points to a rather small shift, around −1.0 nm. The theoretical results of all of the shifts and widths obtained here using the liquid simulation combined with quantum mechanics calculations are obtained as an average after using 100 statistically uncorrelated configurations. The reported excitation energy is obtained by the average transition energy and the full width at half maximum is obtained from the standard deviation σ using FWHM = $2\sigma(2\ln2)^{1/2}$. Considering the expected small experimental values all theoretical results may be considered to give good agreement for the spectral shifts and line width, in spite of the lacking of any consideration of the
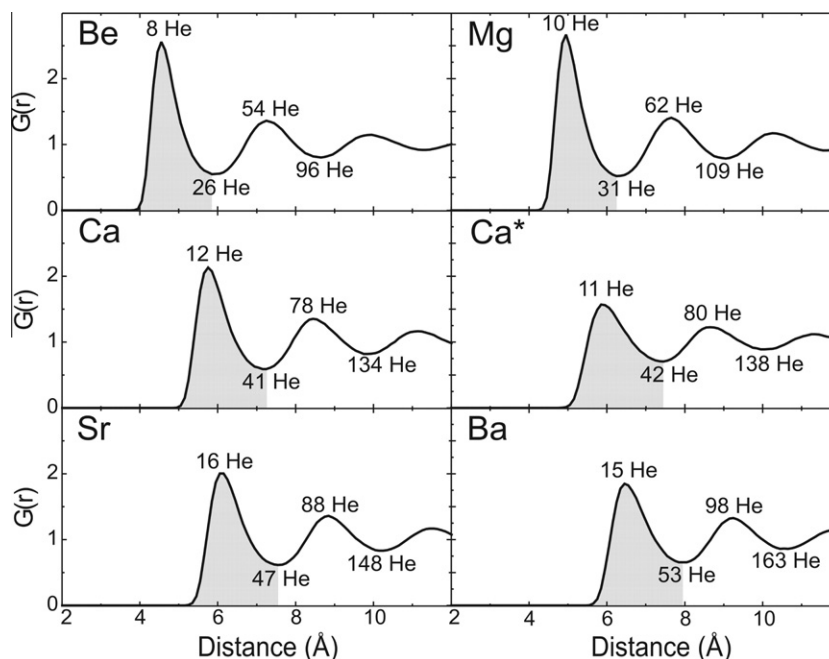
Figure 1. The radial distribution function between the alkaline earth and helium atoms. For Be, Mg, Ca, Sr and Ba the potential LK [40] is used. Ca*, denote also the Ca atom but using the CRSP [41] potential. All graphs are in the same scale.

Table 1
Excitation line shift and width of Be in liquid helium environment.

Potential	Functional	Free (nm)	Shift (nm)	FWHM (nm)
LK CCSD(T)	O3LYP	247.72	−2.15	3.6
	PBE1PBE	248.64	−1.36	2.1
LK CCSD	O3LYP	247.72	−0.75	3.41
	PBE1PBE	248.64	−0.58	1.8
Experimental results [50]		234.86	−0.96	1.70

near degeneracy between the $2s^2$ and $2p^2$ configurations. All results thus predict a spectral shift within 1–2 nm with a width of ∼2 nm.

Now we consider the other alkaline earth atoms. The radial distribution functions obtained from the MC simulation are all shown in Figure 1. In all cases three solvation shells are seen up to the cut-off limit. For Mg–He we used the LK potential [40] and the first solvation shell starts at 4.3 Å, shows a maximum at 5.0 Å and ends at 6.3 Å, comprising a total of 31 surrounding He atoms. Similar results are obtained for Ca–He, Sr–He and Ba–He and the total number of He atoms in the maxima and in the solvation shells are shown for every case, in Figure 1. It is possible to note some systematic trends both in feature and number of He atoms in the first solvation shell. The solvation shells start respectively at 5.0 Å and end at 7.2 Å with the maximum at 5.8 Å for Ca–He, at 5.3 Å and end at 7.6 Å with the maximum at 6.1 Å for Sr–He, at 5.6 Å and end at 8.0 Å with the maximum at 6.5 Å for Ba–He having the total number of He atoms as 41, 47 and 53 in respective cases. For Ca–He the results with the CRSP pair potential [41] gives 42 as the number of He atoms in the first solvation shell, the other features remaining essentially the same. The results for the transition shift and the corresponding width for the low-lying excitations are displayed in Table 2. As mentioned two hybrids functionals O3LYP and PBE1PBE with different basis sets are used and the results are compared with the existing experimental data. The experimental absorption transition for the free atom is at 422.7 nm in the case of Ca. This compares favorably with the O3LYP result but differs by 0.12 eV from the PBE1PBE results. This is within the expectation that TDDFT cannot

produce results with better reliability than ∼0.1 eV. Here we focus in transition energy shifts. Considering the same transition in helium environment two results are obtained depending on the potential used in the simulation. For the potential based on the CRSP parameters [41] we obtain using the same O3LYP functional a blue shift of −4.7 nm, in good agreement with the experimental value of −2.7 nm. This could be compared with the value obtained from the bubble model estimate [11] of −21.5 nm. It is clear that the present method represents a considerable improvement over previous theoretical approaches. The corresponding results obtained with the PBE1PBE functional are also in very good agreement but the analysis of these results seem to indicate that the CRSP parameters for the Ca–He potential provide a slightly better representation than the LK potential. For the case of Sr the calculated result using the O3LYP functional gives the result of −3.3 nm for the blue shift, in sharp agreement with the experimental value. Similar picture is obtained for the case of Ba, where the calculated shifts are ca. −6 nm, compared with the experimental value of −4.3 nm. In contrast the bubble model results for Sr and Ba are again very large; i.e. −25 nm and −33.5 nm, respectively. In all such cases we find the PBE1PBE functional with *def2-qzvp* basis set for the central atom yield consistent results in very good agreement with experimental values. Only in the Ba–He system the estimated width is in better agreement with the result obtained from O3LYP/*def2-qzvp* calculation. For the Ca–He system the CRSP pair potential [41] yields marginally better results. Table 2 also shows the calculated results for the widths, in every case. As it can be seen these are also found to be in very good agreement with the experimental results.

The natural inhomogeneous broadening in the liquid environment is derived from the ensemble of different configurations of the three $s \rightarrow p$ transitions due to the breakdown of the degeneracy of the np orbital. No attempt has been made so far to understand the separate contribution of the $s \rightarrow p$ splitting. We thus show in Figure 2 the Gaussian distribution of the calculated transition energies in the case of the Sr–He system. The explicit contribution of the orbital splitting to the total broadening is also shown in Figure 2. The three components shown in Figure 2 correspond to the three transitions calculated and they are separated by the energy

Table 2
Excitation line shift and line width of the alkaline earth atom R in liquid helium environment.

R Transition	Potential	Functional	Free (nm)	Shift (nm)	FWHM (nm)
Mg3s^2→3s3p:^{1}P	LK [40]	O3LYP	298.81	−6.7	6.6
		PBE1PBE	291.82	−4.9	4.0
	Experimental results		285.17[b]	−3.7 ± 0.5[b]	6.5 ± 0.5[b]
	Previous theoretical results			−6.93[a]	9.0[a]
Ca4s^2→4s4p:^{1}P	CRSP[41]	O3LYP	423.30	−4.7	9.5
		PBE1PBE	406.71	−4.0	5.3
	LK [40]	O3LYP	423.30	−9.6	9.3
		PBE1PBE	406.71	−6.3	5.4
	Experimental results		422.67[c]	−2.65 ± 0.5[c]	4.75 ± 0.5[c]
	Previous theoretical results			−5.67[a] −21.50[c] −9.4[d] −2.8[d]	7.3[a] 5.6[c] 3.2[d] 1.75[d]
Sr5s^2→5s5p:^{1}P	LK [40]	O3LYP	465.02	−3.3	7.2
		PBE1PBE	449.96	−4.1	4.3
	Experimental results		460.73 [c]	−3.3 ± 0.5[c]	5.95 ± 0.5[c]
	Previous theoretical results			−4.43[a] −25.0[c]	4.3[a] 6.3[c]
Ba6s^2→6s6p:^{1}P	LK [40]	O3LYP	538.98	−6.5	9.2
		PBE1PBE	517.31	−6.2	5.1
	Experimental results		553.55 [c]	−4.3 ± 0.5[c] −6.55[e]	8.5 ± 0.5[c] 7.0[e]
	Previous theoretical results			−7.55[a] −33.5[c] −37.0[c]	8.1[a] 7.6[c] 11.0[c]

[a] Ref. [29].
[b] Ref. [16].
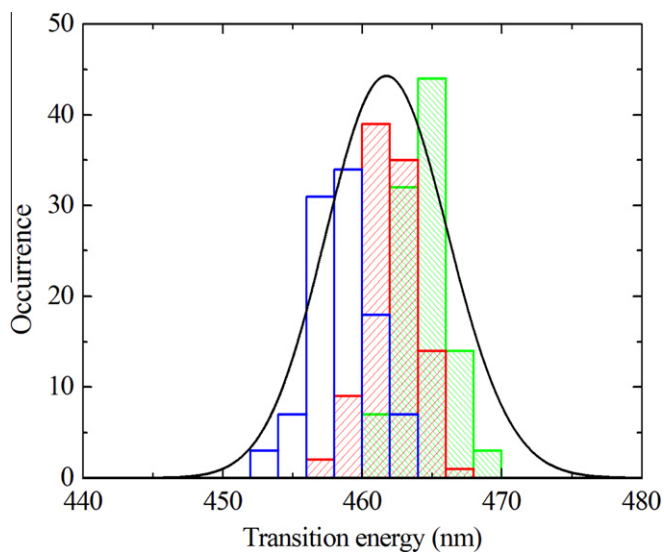[c] Ref. [11].
[d] Ref. [26].
[e] Ref. [28].

Figure 2. The GAUSSIAN distribution of the calculated transition energies of Sr in liquid helium. Also shown are the separate contributions of the three s–p transitions.
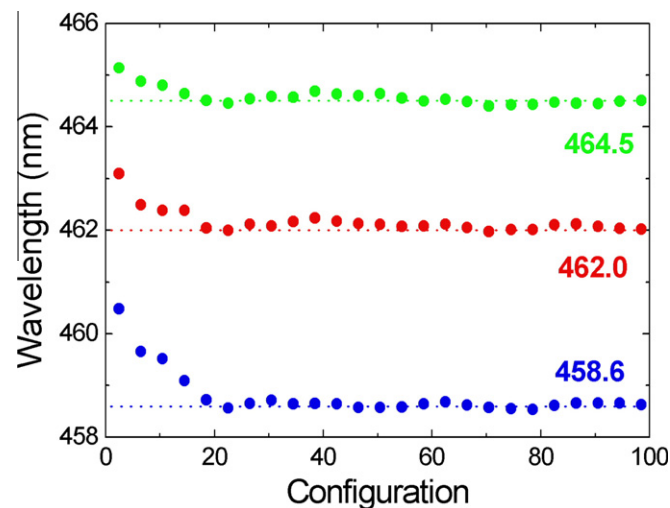

Figure 3. Convergence of the calculated transition wavelength of Sr in liquid helium with respect to the number of configurations used. These are the separate contributions of the three s–p transitions.

positioning in each configuration. No label was attributed to each transition (p_x, p_y and p_z). So they may change in order from one configuration to another, but always three different energies coming from the excitation and they were averaged as the lower- middle- and higher-energy component for each configuration. The convergence of the calculated results reported with respect to the sampling can be seen in Figure 3. In general, Table 2 shows a very good agreement between our calculated values and the experimental transition energies and widths. For instance, in the case of Sr, using the O3LYP functional, we obtain a transition shift of −3.3 nm and a FWHM of 7.2 nm. These compare very well with the experimental values of −3.3 and 6.0 nm, respectively.

Finally we consider now the use of optimized clusters for obtaining the spectral properties of foreign atoms in liquid helium. Theoretical estimates of the spectral line shifts of alkali atoms Rb and Cs embedded in liquid helium are available with a surrounding model cluster of 14 atoms placed at the corners and over the face of a cube with the alkali atom at the center [31,32]. Geometry optimization and total energy estimates for the ground and first excited states have been performed using density functional theory with relativistic correction. Such calculations have been performed for all the systems studied here. To have a general overview of the success of the non-relativistic model cluster using similar basis sets and correlation functional Table 3 displays the results. We note that in general the results systematically overestimate the spectral shift. It may be noted that the distances, R_{min}, from the central R atom to the He atoms are consistently shorter than the maximum of first solvation shell. This is consistent because in the liquid phase the average distance is expected to be larger due to the temperature effect. But the results with the O3LYP functional with the def2-qzvp basis set yields consistently good results for the shifts but cannot describe the inhomogeneous broadening. In comparing

Table 3
Spectral line shift of alkaline earth atom under liquid helium in optimized minimum-energy configuration. R_{min} denotes the R–He distance of the cluster energy minimum.

R	Functional	R_{min} (Å)	Free (nm)	Shift (nm)
Mg	O3LYP	4.92	298.81	−3.4
	PBE1PBE	4.59	291.82	−6.8
	Experimental result [16]		285.17	−3.7 ± 0.5
Ca	O3LYP	5.58	423.30	−4.8
	PBE1PBE	5.27	406.71	−9.0
	Experimental result [11]		422.67	−2.65 ± 0.5
Sr	O3LYP	5.76	465.02	−5.1
	PBE1PBE	5.48	449.96	−8.9
	Experimental result [11]		460.73	−3.3 ± 0.5
Ba	O3LYP	5.58	538.98	−8.8
	PBE1PBE	5.77	517.31	−10.9
	Experimental result [11]		553.55	−4.3 ± 0.5

the maximum of the radial distribution function in the liquid case one notes that it increases systematically from 5.0 Å in the case of Mg to 5.8, 6.1 and 6.5 Å, for Ca, Sr and Ba, respectively. This trend is reproduced in the case of the calculated values of R_{min}, only by PBE1PBE as seen in Table 3.

4. Conclusions

A combined and sequential use of Monte Carlo simulation and quantum mechanical calculations is a viable procedure for the calculation of the spectral changes in atomic excitations inside liquid helium. In this work consistent results are obtained for all alkaline atoms considered. This includes not only the spectral shift due to the interaction with the He environment but also the associated line broadening that in this case has three contributing transitions, due to the splitting of the np orbital. For comparison, the cluster model with optimized minimum-energy structure is also considered. Because of the small temperature of liquid helium this can also give results in reasonable agreement. But from construction, this is of limited value for estimating the line widths. This combined use of quantum mechanics and statistical mechanics is also an important method for the estimation of the emission line shifts provided reasonable estimates of the excited state pair potentials are available.

Acknowledgments

References

[1] B. Tabbert, H. Günther, G. zuPutlitz, J. Low. Temp. Phys. 109 (1997) 653.
[2] A.L. Fetter, The Physics of Liquid and Solid Helium, Part I, in: K.H. Bennemann, J.B. Ketterson (Eds.), Wiley, New York, 1976.
[3] J. Wilks, D.S. Betts, An Introduction to Liquid Helium, Clarendon Press, Oxford, 1987.
[4] Y. Takahashi, K. Sano, T. Kinoshita, T. Yabuzaki, Phys. Rev. Lett. 71 (1993) 1035.
[5] H. Bauer, M. Haussmann, R. Mayer, H.J. Reyher, E. Weber, A. Winnacker, Phys. Lett. A 110 (1985) 279.
[6] E.B. Gordon, V.V. Khmelenko, A.A. Pelmenev, E.A. Popov, O.F. Pugachev, A.F. Shestakov, Chem. Phys. 170 (1993) 411.
[7] R.A. Ferrel, Phys. Rev. 108 (1957) 167.
[8] G. De Toffol, F. Ancilotto, F. Toigo, J. Low Temp. Phys. 102 (1996) 381.
[9] S.I. Kanorski, M. Arndt, R. Dziewior, A. Weis, T.W. Hänsch, Phys. Rev. B 50 (1989) 6296.
[10] H. Bauer, M. Beau, A. Bernhardt, B. Friedel, H.J. Reyher, Phys. Lett. A 137 (1989) 217.
[11] H. Bauer, M. Beau, B. Friedl, C. Marchand, K. Miltner, H.J. Reyher, Phys. Lett. A 146 (1990) 134.
[12] J.H.A. Beijersbergen, Q. Hui, M. Takami, Phys. Lett. A 181 (1993) 393.
[13] B. Tabbert, M. Beau, H. Günther, W. Häubler, C. Hönninger, K. Meyer, B. Plagemann, Z. Phys. B 97 (1995) 425.
[14] H. Günther, M. Foerste, C. Hönninger, Z. Phys. 98 (1995) 395.
[15] Q. Hui, J.L. Persson, J.H.M. Beijersbergen, M. Takami, Z. Phys. B 98 (1995) 353.
[16] Y. Moriwaki, N. Morita, Eur. Phys. J. D 5 (1999) 53.
[17] F. Dalfovo, Z. Phys. D 29 (1994) 61.
[18] F. Ancilotto, E. Cheng, M.W. Cole, F. Toigo, Z. Phys. B 98 (1995) 323.
[19] J. Dupont-Roc, Z. Phys. B 98 (1995) 383.
[20] J. Jspann, Z. Phys. B 98 (1995) 405.
[21] A.P. Hickman, W. Steets, N.F. Lane, Phys. Rev. B 12 (1975) 3705.
[22] A.P. Hickmann, N.F. Lane, Phys. Rev. Lett. 26 (1971) 1216.
[23] J.P. Hansen, E.L. Pollock, Phys. Rev. A 5 (1972) 2214.
[24] W. Steets, A.P. Hickman, N.F. Lane, Chem. Phys. Lett. 28 (1974) 31.
[25] J. Wisdom, T.W. Hartquist, N.F. Lane, Phys. Rev. B 14 (1976) 4205.
[26] M. Beau, H. Günther, Z. Phys. B 101 (1996) 253.
[27] S. Kanorsky, A. Weis, M. Arndt, R. Dziewior, T.W. Hänsch, Z. Phys. B 98 (1995) 371.
[28] T. Yabuzaki, A. Fujisaki, K. Sano, T. Kinoshita, Y. Takahashi, Atomic Physics B (1992), H. Walther, T.W. Hänsch (Eds.), North Holland, New York.
[29] J.Z. Tang, M. Kimura, I. Shimamura, Chem. Phys. Lett. 256 (1996) 327.
[30] B. Saha, R. Fukuda, H. Nakatsuji, P.K. Mukherjee, Theor. Chem. Acc. 118 (2007) 437.
[31] J. Anton, P.K. Mukherjee, B. Fricke, S. Fritzsche, J. Phys. B At. Mol. Opt. Phys. 40 (2007) 2453.
[32] J. Anton, B. Fricke, P.K. Mukherjee, S. Fritzsche, Phys. Lett. 372 (2008) 4462.
[33] K. Coutinho, S. Canuto, P.K. Mukherjee, B. Fricke, Spectroscopy of Atoms in Liquid Helium Environment: A Theoretical Perspective in Advances in the Theory of Atomic and Molecular Systems: Dynamics, Spectroscopy, Clusters, and Nanostructures, Vol. 20, Springer Book Series 'Progress in Theoretical Chemistry and Physics, P. Piecuch, J. Maruani, G. Delgado-Barrio, S. Wilson (Eds.), (2009) pp. 183–200.
[34] V. Ludwig, P.K. Mukherjee, K. Coutinho, S. Canuto, Phys. Rev. A 72 (2005) 062714.
[35] K. Coutinho, S. Canuto, Adv. Quantum Chem. 28 (1997) 89.
[36] K. Coutinho, S. Canuto, J. Chem. Phys. 113 (2000) 9132.
[37] R.C. Barreto, K. Coutinho, H.C. Georg, S. Canuto, Phys. Chem. Chem. Phys. 11 (2009) 1388.
[38] L. Modesto-Costa, K. Coutinho, P.K. Mukherjee, S. Canuto, Phys. Rev. A 83 (2010) 042515.
[39] N. Metropolis, A.W. Rosenbluth, A.N. Rosenbluth, A.H. Teller, E. Teller, J. Chem. Phys. 21 (1953) 1087.
[40] C.C. Lovallo, M. Klobukowski, Chem. Phys. Lett. 373 (2003) 439.
[41] E. Czuchaj, F. Rebentrost, H. Stoll, H. Preuss, Chem. Phys. 138 (1989) 303.
[42] K. Coutinho, S. Canuto, M.C. Zerner, J. Chem. Phys. 112 (2000) 9874.
[43] W.R. Rocha, K. Coutinho, W.B. de Almeida, S. Canuto, Chem. Phys. Lett. 335 (2001) 127.
[44] N.C. Handy, A.J. Cohen, Mol. Phys. 99 (2001) 607.
[45] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 78 (1997) 1396.
[46] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 7 (2005) 3297.
[47] M. Kaupp, P.V. Schleyer, H. Stoll, H. Preuss, J. Chem. Phys. 94 (1991) 1360.
[48] K. Coutinho, S. Canuto, DICE (version 2.9): A general Monte Carlo program for liquid simulation, University of São Paulo (2009).
[49] M. J. Frisch, et al. GAUSSIAN 09, Revision A.1, GAUSSIAN, Inc., Wallingford CT, (2009).
[50] M. Foereste, G. Zu Putlitz: private comunication.