J. Phys. Chem. A **2002,** *106,* 3197−3201

Accuracy of Theoretical Potential Energy Profiles along Proton-Transfer Coordinate for $XH-NH_3$ (X = F, Cl, Br) Hydrogen-Bonded Complexes

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Received: October 18, 2001; In Final Form: February 1, 2002

The study of ab initio potential energy curves along the proton-transfer coordinate in $XH-NH_3$ (X = F, Cl, Br) hydrogen-bonded complexes is reported. Equilibrium geometries, harmonic vibrational frequencies, one-dimensional energy profiles, and anharmonic proton stretching frequencies have been calculated at B3-LYP/6-311++G(d,p), MP2/6-311++G(d,p), MP2/6-311++G(2df,2pd), and CCD/6-311++G(2df,2pd) levels of theory. The results have been compared to more accurate CCSD(T)/6-311++G(2df,2pd) values. It has been found that the structures and most of the harmonic vibrational frequencies of the complexes agree well, but the proton stretching frequencies differ significantly. These differences are enhanced when anharmonicity along the proton transfer coordinate is taken into account, and even small inaccuracies in the PES cause large errors in the computed frequencies. These results show that the proper treatment of electron correlation is extremely important for the correct description of anharmonic energy profiles in hydrogen-bonded complexes.

1. Introduction

The properties of hydrogen-bonded systems strongly depend on the shape of the potential energy surface (PES) along the proton-transfer coordinate. Ammonia−hydrogen halides are interesting examples of neutral type hydrogen-bonded complexes for which infrared (IR) and/or microwave (MW) spectroscopic investigations in the gas phase have been reported.[1−5] In agreement with theory,[6−12] their PES has a single minimum with the HX bond only slightly elongated compared to free molecule. On the other hand, the big discrepancies observed between the theoretical[10,11] and the matrix-isolated experimental[13−23] vibrational frequencies need to be explained: they may be due to the failure of the harmonic approximation, to the inherent strong anharmonicity of the proton stretching $\nu(H-X)$ mode, to the large coupling with the intermolecular stretching $\nu(X-H-N)$, to the level of correlation treatment, and to the nonnegligible matrix effects.

Two approaches have been already applied[24−28] to the study of anharmonic frequencies for ammonia−hydrogen halide complexes. For $XH-NH_3$ (X = F, Cl, Br), Del Bene et al.[24−27] constructed one- V(r(HX)) and two-dimensional V(r(HX), r(HN)) PESs at the MP2/6-31+G(d,p) level of theory. The matrix effect was included either with the explicit treatment of rare gas atoms or by modifying the force field. The vibrational eigenvalues were then calculated variationally. They showed that the inclusion of one-dimensional anharmonicity causes a substantial lowering of the $\nu(H-X)$ frequency and improves the agreement with available experimental data, whereas the couplings between the fast and the slow hydrogen-bonded modes additionally redshifts proton stretch frequency. Chaban et al.[28] performed full anharmonic, taking into account all modes, gas-phase studies of $ClH-NH_3$ complex using the correlation-corrected vibrational self-consistent field (CC−VSCF)[29,30] approach with similar results. The most accurate calculations of anharmonic vibrational frequencies and PESs for these complexes were performed at the MP2 level,[24−28] which was believed to be sufficiently accurate for this class of problems, like for instance for $(H_2O)_n$ and $Cl^-(H_2O)_n$[29,31] neglect of anharmonicity yields errors much larger than improper description of correlation energy. However, it is interesting to check the accuracy of the MP2 results.

In this paper, the structures, the harmonic spectra, and the potential energy curves along proton-transfer pathway calculated for $XH-NH_3$ (X = F, Cl, Br) complexes at different levels of theory are presented. The aim of this study is to determine the accuracy of different ab initio energy profiles. To concentrate on this subject, environmental and coupling effects are neglected and only calculations related to the gas phase are performed. Hence, to show the relation between the shape of PES and the proton-stretch frequency, anharmonic $\nu(H-X)$ frequencies are computed with a simple one-dimensional model.

2. Computations

When, for investigation of PESs, calculations of electronic energies far from equilibrium geometry are required, nondynamical correlation energy may become important. Benchmark studies[32,33] have shown that the coupled cluster method including single, double, and, noniteratively, triplet excitations (CCSD(T))[34−38] is sufficient and gives energies in good agreement with full configuration interaction (CI) energies even for the geometries strongly distorted from equilibrium. Moreover for all $XH-NH_3$ complexes, in the region of the PES investigated, CCSD(T) satisfies the T1 diagnostic of Lee and co-workers.[39] For these reasons, we take the CCSD(T) method as our reference, to test the accuracy of other ab initio surfaces.

All ab initio calculations were performed using the Gaussian 98[40] package of computer codes. The geometry optimization and all energy grid calculations were performed for the XH−

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10.1021/jp013891l CCC: $22.00

TABLE 1: Computed and Experimental Parameters of $XH-NH_3$ Complexes, Bond Lengths in Angstroms and Angles in Degrees

		R(X−N)	r(HX)	r(HN)	θ(HNH)
$FH-NH_3$	B3-LYP/6-311++G(d,p)	2.662	0.947	1.01	107.65
	MP2/6-311++G(d,p)	2.651	0.948	1.015	106.82
	MP2/6-311++G(2df,2pd)	2.637	0.951	1.011	107.19
	CCD/6-311++G(2df,2pd)	2.665	0.941	1.011	107.11
	CCSD(T)/6-311++G(2df,2pd)	2.649	0.946	1.014	107.04
	expt	2.697[a]			
$ClH-NH_3$	B3-LYP/6-311++G(d,p)	3.144	1.325	1.010	107.82
	MP2/6-311++G(d,p)	3.130	1.312	1.016	106.74
	MP2/6-311++G(2df,2pd)	3.079	1.319	1.012	107.32
	CCD/6-311++G(2df,2pd)	3.176	1.303	1.011	107.11
	CCSD(T)/6-311++G(2df,2pd)	3.142	1.311	1.014	106.99
	expt	3.137[b]			
$BrH-NH_3$	B3-LYP/6-311++G(d,p)	3.297	1.471	1.011	107.92
	MP2/6-311++G(d,p)	3.268	1.460	1.016	106.83
	MP2/6-311++G(2df,2pd)	3.210	1.472	1.012	107.52
	CCD/6-311++G(2df,2pd)	3.350	1.448	1.011	107.16
	CCSD(T)/6-311++G(2df,2pd)	3.303	1.458	1.014	107.07
	expt	3.255[c]			

[a] Reference 5. [b] References 2 and 4. [c] Reference 3.

NH_3 complexes with the CCSD(T) method and the 6-311++G(2df,2pd)[41−44] basis set. Structures, harmonic vibrational spectra, and PES were also calculated for all $XH-NH_3$ complexes at the density functional (DFT), second-order Møller−Plesset (MP2),[45,46] and coupled clusters with double excitations (CCD)[47] levels of theory using various basis sets ranging from 6-311++G(d,p)[41−43] to 6-311++G(2df,2pd)). In DFT calculations, a slightly modified[48] three-parameter, hybrid B3-LYP, functional has been used. To obtain one-dimensional potential energy curves, only the proton position in the hydrogen bridge was allowed to vary, whereas all remaining geometry parameters were kept fixed at the corresponding to theoretical equilibrium values. The ab initio energies were fitted[49] (RMSQ < 10 cm^{-1}) with a sixth order polynomial V(r(HX)), and the vibrational levels were calculated by a Lanczos algorithm.[50,51]

3. Results and Discussion

The main purpose of this work is to compare the proton stretching frequencies of hydrogen-bonded complexes computed using different computational methods: we concentrate only on the ab initio energy profiles along the proton transfer pathway neglecting environmental and coupling effects. Because the latter are generally important for the agreement between experiment and theory, the detailed comparison with the experimental frequencies remains outside the scope of this work. The main conclusions on the relative accuracy of the potential energy profiles are presumably general and apply to all H−X bonds with strong anharmonic effects.

For $XH-NH_3$ complexes, there are no experimental data to be compared directly with theory. For all complexes, only the hydrogen bridge bond lengths have been obtained experimentally from rotational spectroscopy.[2−5] The experimental values represent vibrationally averaged R_0, whereas the computed ones correspond to the global energy minimum position R_e, making some discrepancies unavoidable. In addition, the frequencies of the isolated complex cannot be compared directly with low-temperature experimental data because of the neglect of matrix effects.

Taking CCSD(T)/6-311++G(2df,2pd) as a reference, we start our analysis by comparing the equilibrium geometry parameters in Table 1 with the available experimental data. All methods predict molecular type hydrogen-bonded structures for all investigated ammonia hydrogen halide complexes, in agreement with previous experimental[1−5] and computational[6−12] studies. The R(F−N) distance is estimated to be shorter (up to 0.06 Å) than the experimental value; the hydrogen bridge distance computed for $ClH-NH_3$ agrees with the experiment within ±0.06 Å; with the exception of MP2/6-311++G(2df,2pd), all R(Br−N) distances are estimated to be longer than experimental data, with maximum difference of 0.1 Å for CCD/6-311++G(2df,2pd). We next note the large variations of the bond length of the hydrogen bond bridge computed by different methods. The magnitude of this effect increases in order $FH-NH_3$, $ClH-NH_3$, and $BrH-NH_3$ with a maximum difference of 0.1 Å. For all complexes, MP2/6-311++G(2df,2dp) shows the largest deviations from the CCSD(T) values, with hydrogen bond distances shorter by 0.012, 0.063, and 0.093 Å for X = F, Cl, and Br, respectively. By contrast, the MP2/6-311++G(d,p) hydrogen bond lengths agree well with the CCSD(T): the R(X−N) is only 0.002 Å longer in $FH-NH_3$ and 0.012 and 0.035 Å shorter for $ClH-NH_3$ and $BrH-NH_3$ respectively. Finally we note that B3-LYP/6-311++G(d,p) geometry is comparable to the much more computationally demanding CCD/6-311++G(2df,2pd).

We move next to the harmonic frequencies in Table 2 noting that the MP2/6-311++G(d,p) and CCSD(T)/6-311++G(2df,2dp) proton stretching harmonic frequencies of $FH-NH_3$ are in close agreement as found for the equilibrium geometries. For the high computational cost of CCSD(T)/6-311++G(2df,2dp), the MP2/6-311++G(d,p) harmonic frequencies are believed to be sufficiently accurate for this comparison. On this ground, the harmonic frequencies calculated at different levels of theory are easily classified into three groups: the hydrogen-bonded dimer stretch ν(X−H−N) and all but the antisymmetric stretch intermolecular modes of ammonia are nearly insensitive to the theoretical method used for computations and have maximum deviations of 30 cm^{-1}. Slightly larger differences were found for the ammonia antisymmetric bend and the hydrogen bond bending (β(X−H−N)) and wagging (γ(X−H−N)) modes, but also in these cases, all methods predict values that agree within 100 cm^{-1}. The differences are much larger for the proton-stretching frequency, 192, 204, and 296 cm^{-1} for $FH-NH_3$, $ClH-NH_3$, and $BrH-NH_3$ respectively, proving the extreme sensitivity of the mode to the level of the orbital description and of the correlation treatment.

TABLE 2: Harmonic Vibrational Frequencies (cm^{-1}) of XH−NH$_3$ Complexes

		$\nu_{as(3)}$(NH$_3$)	$\nu_{s(1)}$(NH$_3$)	ν(H−X)	$\alpha_{as(4)}$(NH$_3$)	$\alpha_{s(2)}$(NH$_3$)	β(X−H−N)	γ(X−H−N)	ν(X−H−N)
		E	A1	A1	E	A1	E	E	A1
FH−NH$_3$	B3-LYP/6-311++G(d,p)	3658	3544	**3455**	1701	1168	986	285	261
	MP2/6−311 ++G(d,p)	3663	3526	**3479**	1644	1175	989	278	265
	MP2/6−311 ++G(2df,2pd)	3668	3530	**3427**	1671	1147	1009	277	277
	CCD/6-311++G(2df,2pd)	3658	3532	**3619**	1689	1166	979	273	262
	CCSD(T)/6-311++G(2df,2pd)	3628	3498	**3521**	1685	1163	1002	337	284
ClH−NH$_3$	B3-LYP/6-311++G(d,p)	3661	3541	**2379**	1701	1139	773	254	177
	MP2/6−311 ++G(d,p)	3652	3512	**2523**	1638	1170	741	242	181
	MP2/6−311 ++G(2df,2pd)	3649	3528	**2510**	1701	1155	714	219	165
	CCD/6-311++G(2df,2pd)	3657	3530	**2583**	1688	1137	704	216	164
BrH−NH$_3$	B3-LYP/6-311++G(d,p)	3662	3541	**2052**	1698	1132	721	238	141
	MP2/6−311 ++G(d,p)	3654	3509	**2134**	1631	1154	697	223	145
	MP2/6−311 ++G(2df,2pd)	3665	3519	**2003**	1664	1116	785	228	148
	CCD/6-311++G(2df,2pd)	3657	3528	**2299**	1686	1130	642	201	131

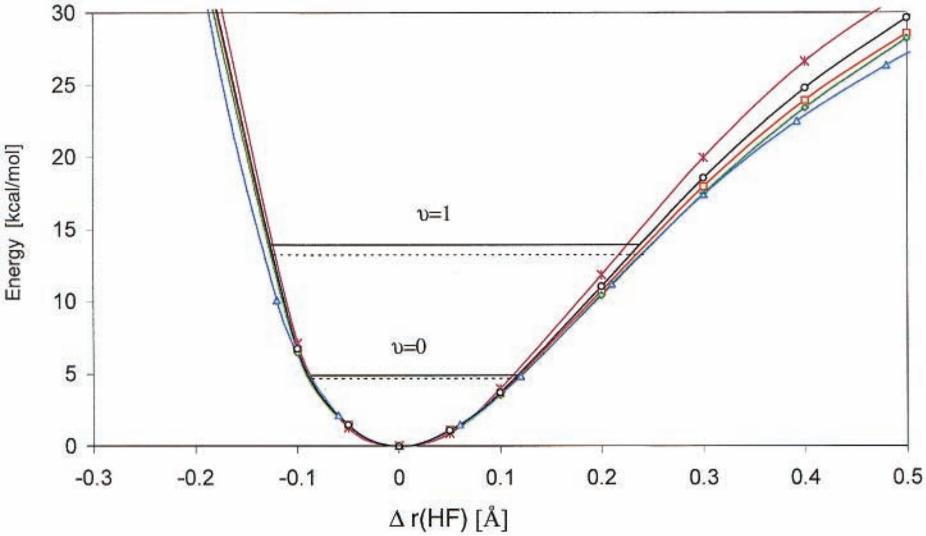

Figure 1. Potential curves along proton-transfer coordinate (Δr(HF) = r(HF) − r_e(HF)) for FH−NH$_3$ calculated at B3-LYP/6-311++G(d,p) (△, blue), MP2/6-311++G(d,p) (□, red), MP2/6-311++G(2df,2pd) (◇, green), CCD/6-311++G(2df,2pd) (*, violet), and CCSD(T)/6-311++G(2df,2pd) (○, black) levels of theory. The first two vibrational levels calculated at CCSD(T)/6-311++G(2df,2pd) (solid line) and MP2/6-311++G(2df,2pd) (dotted line) are shown.

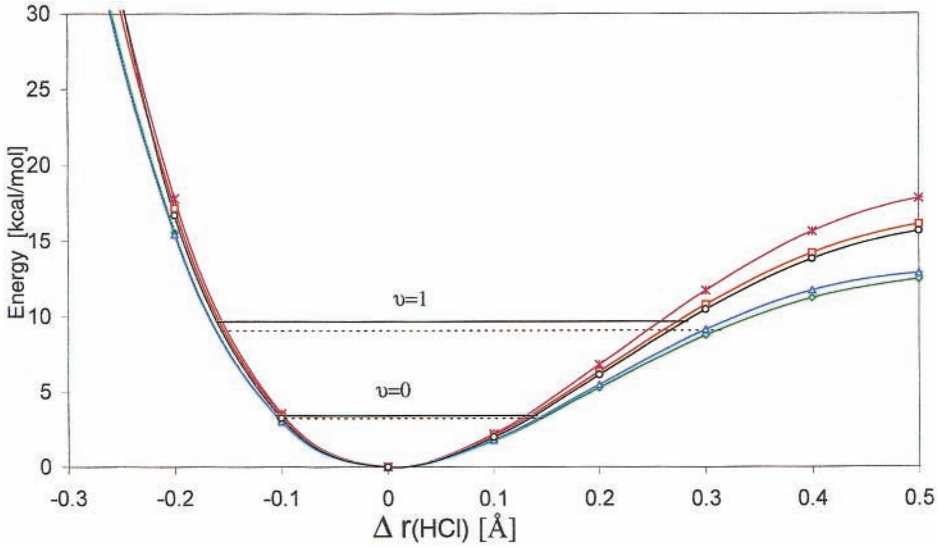

Figure 2. One-dimensional potential curves along proton-transfer coordinate for ClH−NH$_3$. The meaning of the marks is explained in the caption of Figure 1.

The potential energy profiles along proton-transfer coordinate are shown in Figures 1−3 for FH−NH$_3$, ClH−NH$_3$, and BrH−NH$_3$ complexes, respectively. Our results show that all methods predict strongly anharmonic potential energy curves with a single minimum corresponding to the molecular hydrogen-bonded structure. In all pictures, the first two anharmonic vibrational levels calculated from the CCSD(T)/6-311++G(2df,2dp) potential are shown as solid lines and compared to the vibrational levels, dotted lines, from the MP2/6-311++G(2df,2pd) potential.

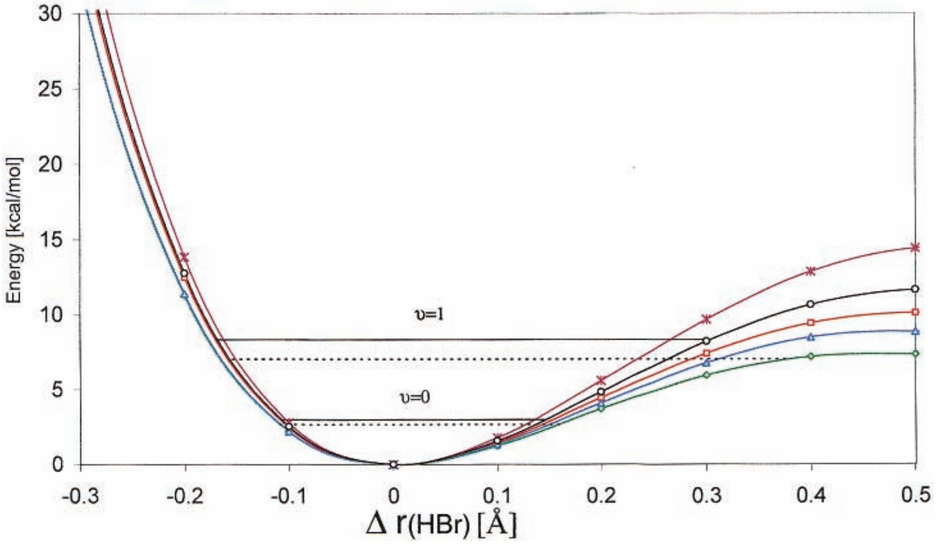

Figure 3. One-dimensional potential curves along proton-transfer coordinate for BrH−NH$_3$. The meaning of the marks is explained in the caption of Figure 1.

TABLE 3: Anharmonic Proton Stretching Frequencies (cm^{-1}) of the XH−NH$_3$ Complexes.

	ν(H−F)	ν(H−Cl)	ν(H−Br)
B3-LYP/6-311++G(d,p)	2998	2005	1656
MP2/6−311 ++G(d,p)	3117	2193	1796
MP2/6−311 ++G(2df,2pd)	2991	2029	1525
CCD/6-311++G(2df,2pd)	3297	2285	2014
CCSD(T)/6-311++G(2df,2pd)	3156	2180	1872

For all complexes, the vibrational ground-state region is well represented by all methods without significant differences in the profile and in the $\upsilon = 0$ energies. All methods but CCD yield potentials flatter than the CCSD(T). The effect is almost negligible for FH−NH$_3$ but increases for ClH−NH$_3$ and BrH−NH$_3$. In the region of the first vibrational level, more significant differences start to become apparent. It is confirmed that CCD potentials are steeper than CCSD(T) and all other potentials flatter. For all complexes, MP2/6-311++G(d,p) provides the closest approximation to the CCSD(T) potential in agreement with previous analysis of the equilibrium geometries. The deviations of the B3-LYP/6-311++G(d,p) and MP2/6-311++G-(2df,2pd) potentials from our reference are more pronounced.

Vibrational variational calculations were performed to include the effects of anharmonicity on the computed spectra. The resulting one-dimensional anharmonic proton stretch frequencies are listed in Table 3. Even for the FH−NH$_3$ complex, the difference between the values of ν(H−F) frequency from the steepest (CCD) and the flattest (MP2/6-311++G(2df,2p)) potential is larger than 300 cm^{-1}. For the ClH−NH$_3$ complex, the difference is similar, for BrH−NH$_3$ much larger, approximately 500 cm^{-1}. By comparison, the differences of the harmonic frequencies in Table 2 do not exceed 300 cm^{-1}. Our interpretation of the results, showing clearly that different ab initio methods give rather different potentials for the proton-stretching mode, is as follows. All methods used for this investigation, including the relevant amount of correlation energy, are considered as sufficiently accurate for hydrogen-bonded systems. Yet, for the faithful representation of the H−X anharmonicity, geometries strongly distorted from equilibrium need to be considered. The electronic state being not anymore adequately described by single configuration wave functions, the effects of nondynamic correlation are enhanced and the limitations of the methods such as MP2 or CCD, which neglect entirely this energy contribution, become apparent. For the hydrogen-bonded complexes investigated in this paper, the T1 diagnostic is satisfied and the CCSD(T) have been already found[32,33] to agree well with full CI even in the case of substantial nondynamic correlation effects. Using MP2 with the smaller basis set 6-311++G(d,p), the errors in the treatment of dynamical and nondynamical correlation energy accidentally compensate, and anharmonic proton stretch frequencies are in reasonable agreement with CCSD(T). The ν(H−X) frequencies computed with the two methods differ by 39, 13, and 78 cm^{-1} for FH−NH$_3$, ClH−NH$_3$, and BrH−NH$_3$, respectively.

For most hydrogen-bonded systems, highly accurate calculations of many ab initio points are still out of computational limits. On the other hand, theoretical frequencies have been reported in the literature in good agreement with the experiment even without including nondynamic correlation effects. For instance, the CC−VSCF/MP2 vibrational frequencies of $(H_2O)_2$[29] are within 50 cm^{-1} from the experiment. In our opinion, the agreement is due either to a smaller anharmonicity of the potential curves or to a fortuitous cancellation of errors as found in the case of MP2/6-311++G(d,p). This error cancellation suggest a practical recipe to obtain, at a reasonable computational cost, the MP2/6-311++G(d,p) anharmonic frequencies calculations results very close to CCSD(T)/6-311++G(2df,-2pd). For FH−NH$_3$, we found that the difference is negligible (0.002 Å) for geometry and satisfactory (40 cm^{-1}) for proton stretch ν(H−F) frequency.

4. Conclusions

In this work, several ab initio methods, namely, B3-LYP/6-311++G(d,p), MP2/6-311++G(d,p), MP2/6-311++G(2df,-2pd), and CCD/6-311++G(2df,2pd), have been compared to CCSD(T)/6-311++G(2df,2pd). All methods predicts very similar structures and harmonic vibrational frequencies for the complexes with the exception of the proton stretch frequency for which large differences have been observed. These differences are enhanced after including anharmonicity along the proton-transfer coordinate. Such a behavior has been found for all complexes, and its magnitude increases from FH−NH$_3$ to ClH−NH$_3$ to BrH−NH$_3$. For the latter species, the CCD frequencies are more than 500 cm^{-1} higher than MP2/6-311++G(2df,2pd) ones.

These results show that the proper treatment of electron correlation is extremely important for the correct description of anharmonic energy profiles in all hydrogen-bonded complexes. It has been shown how even small inaccuracies in PES account for large errors in computed frequencies. An empirical prescription, MP2 using a reduced basis set of 6-311++G(d,p) orbitals, is suggested to balance the errors in the treatment of the electron correlation terms dynamical and nondynamical and obtain accurate values of the H-bond stretching frequency ν(H−X).

Acknowledgment. This work was enabled by an MINOS grant (to M.B.; EC/TMR program) from CINECA, Casalecchio di Reno, Bologna, Italy. M.B is grateful to the staff of the CINECA for all technical support and hospitality and to Prof. P. Palmieri and Dr. R. Tarroni for suggestions and stimulating discussions. M.B. would like to acknowledge support of the MURST of Italy and the EEC under the RTN Program 7 (Contract No. HPRN-CT-1999-00005). All authors acknowledge the Wrocław Supercomputer Center for providing computer time where some of the calculations were performed.

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