Approaching the theoretical limit in periodic local MP2 calculations with atomic-orbital basis sets: The case of LiH

Denis Usvyat,[1,a)] Bartolomeo Civalleri,[2] Lorenzo Maschio,[2] Roberto Dovesi,[2] Cesare Pisani,[2] and Martin Schütz[1,b)]

[1]*Institute for Physical and Theoretical Chemistry, Universität Regensburg, Universitätsstrasse 31, D-93040 Regensburg, Germany*
[2]*Dipartimento di Chimica IFM, and Centre of Excellence NIS (Nanostructured Interfaces and Surfaces), Università di Torino, via Giuria 5, I-10125 Torino, Italy*

The atomic orbital basis set limit is approached in periodic correlated calculations for solid LiH. The valence correlation energy is evaluated at the level of the local periodic second order Møller-Plesset perturbation theory (MP2), using basis sets of progressively increasing size, and also employing "bond"-centered basis functions in addition to the standard atom-centered ones. Extended basis sets, which contain linear dependencies, are processed only at the MP2 stage via a dual basis set scheme. The local approximation (domain) error has been consistently eliminated by expanding the orbital excitation domains. As a final result, it is demonstrated that the complete basis set limit can be reached for both HF and local MP2 periodic calculations, and a general scheme is outlined for the definition of high-quality atomic-orbital basis sets for solids. © *2011 American Institute of Physics*. [doi:10.1063/1.3595514]

I. INTRODUCTION

In molecular quantum chemistry the hierarchy of approaches, which allow for a systematic improvement of the accuracy of the results, has since long time been established and validated. Indeed, there exists a set of methods, such as Hartree-Fock (HF), second order Møller-Plesset perturbation theory (MP2), coupled cluster with singles doubles, and perturbative triples (CCSD(T)) and so on up to the full configuration interaction, each level implying higher accuracy than the previous one. Furthermore, another main source of error in a theoretical description of the electronic structure of molecules – the one-electron basis set incompleteness – can also to a great extent be reduced and even almost completely eliminated. This can be accomplished either by a balanced expansion of the basis set[1] with a subsequent extrapolation to the complete basis set (CBS) limit,[2] or by means of so called explicitly correlated approaches.[3–7] Many general-purpose computer programs are currently available to the scientific community for *ab initio* calculations of electronic properties of molecules, and following the quantum chemical methodological hierarchy are able to produce highly accurate results, at least for smaller systems. In practical calculations, each new level of accuracy, of course, entails a substantial increase of the computational cost.

Crystals, on the other hand, are 3D packed infinitely large, but periodic systems. For such systems, it is much more difficult to climb up the hierarchy with respect to method and basis set. Implementations of CCSD(T) or better are presently not available in the periodic context (unless in the framework of finite cluster schemes[8–10]). So far, solid state systems

are the domain of density functional theory, which however notoriously lacks the possibility for systematic improvement of the accuracy. As the first post-Hartree-Fock method for crystals periodic MP2 has recently been implemented in the framework of atomic-orbital (AO) (Refs. 11–15) and plane-wave[16,17] basis sets.

Concerning the basis set problem it has been demonstrated very recently that the basis set limit can be reached in periodic HF calculations. For different approaches, i.e., a combined finite cluster/periodic scheme,[18] and purely periodic schemes employing plane waves,[16] and atomic orbitals[19,20] virtually the same HF cohesive energy was obtained at the basis set limit for the LiH crystal (the simplest non-elemental crystalline system: two atoms and four electrons per unit cell, cubic symmetry). In the present work, we address a similar question concerning the same system, but at a higher level of theory: can the basis set limit be reached within a correlated periodic approach employing the AO basis set, in particular, in the context of the periodic local MP2 theory as implemented in the CRYSCOR program.[12–15] An estimate of the basis set limit of the MP2 correlation energy of lithium hydride has recently been presented using the finite cluster hierarchical method.[10,21] Good agreement between this method and a purely periodic plane-wave MP2 approach has also been reported.[16]

The task to approach the basis set limit at the correlated level is substantially more difficult than at the one-electron level. The slow convergence of the correlation energy with basis set size is well-known from molecular (or atomic) studies and originates from the absence of odd-powers of the inter-electron distance in the orbital product expansion of the wave-function. Without such terms the correct description of the Coulomb hole becomes difficult and requires large orbital

a)Electronic mail: denis.usvyat@chemie.uni-regensburg.de.
b)Electronic mail: martin.schuetz@chemie.uni-regensburg.de.

basis sets. A fully periodic AO treatment adds further complications both of fundamental and technical character. Firstly, in periodic systems the non-orthogonality of the AOs can lead to quasi linear dependency among the basis functions for extended basis sets. This effect is known to cause convergence problems and numerical issues in HF calculations. The linear dependency in the basis sets can hinder both the possibility to systematically expand the basis set and to perform basis set extrapolation – techniques, which are routinely employed in molecular calculations. Another issue, preventing the use of the balanced molecular basis set hierarchies, is connected to implementational aspects of the underlying CRYSTAL code, which does not permit orbital basis functions with angular momentum $l \geq 4$ (i.e., beyond f-functions). Such functions are of no relevance for the standard one-electron methods of CRYSTAL. However, high angular momentum functions become essential for describing the Coulomb hole by MP2.

Another obstacle in reaching the limit is the local Ansatz, the local MP2 (LMP2) method is based on. Essentially, it is assumed that correlation effects need to be treated accurately only when the interacting electrons are relatively close to each other, while at larger distances the correlation of their motions can be evaluated approximately or neglected. This approximation is vital for achieving efficiency and linear scaling of the computational costs with unit cell size. A local scheme, which actually results in truncation of the determinantal basis, introduces, however, a certain error, usually small in applications, but becoming relevant for evaluation of the MP2 energy at the basis set limit.

In the present contribution, we address the two issues mentioned above. First, the quality of the basis set is progressively improved by addition of further AO shells to initially chosen relatively rich bases. The problematic parts of the basis sets, containing linearly dependent AOs and thus not tractable at the HF level, are treated only at the correlation stage of the calculation by means of the dual basis set approach.[15,22] Atomic centered high angular momentum functions, which are not available explicitly, are simulated by introducing "bond-centered" functions, i.e., ghost functions located in the middle of the Li-H "bonds." Second, the domain error is removed by performing a series of calculations employing domains of progressively larger size until convergence is reached. Following this approach it is demonstrated that the basis set limit reference value for the valence correlation energy of solid LiH can be reached in the framework of AO-based periodic local correlation methods. This work thus establishes the reliability of local correlation methods for crystals, and in particular of the CRYSCOR program, which nowadays is used in a growing number of applications.

II. SPECIFICATION OF THE COMPUTATIONAL PARAMETERS

In order to concentrate later on the effect of basis set choice and size of the domains of the LMP2 calculations, all other computational parameters are discussed in this section. For all calculations, they have been tightened relative to their default values. At the HF level this concerns the overlap and pseudo-overlap tolerances ITOL1-ITOL5,[23] which regulate

the ranges for the Coulomb and exchange integrals, for which we used 10 10 10 20 100. Furthermore, no integrals have been approximated via the multipole approximation (NOBIPOLA option[23]). A $12 \times 12 \times 12$ k-mesh was applied for the Brillouin zone sampling.

The details of the local MP2 scheme can be found elsewhere.[12,24–26] Here, we briefly describe the main aspects of the method. Both the occupied and virtual spaces are spanned by localized orbitals: orthogonal Wannier functions (WFs), and non-orthogonal (and even redundant) projected atomic orbitals (PAOs), respectively. Wannier functions are generated by the localization-Wannierisation scheme[27] and *a posteriori* symmetrized.[28] PAOs are constructed by projecting the reciprocal space images of AOs onto the virtual space and transforming the result into the direct space.[15] The local approximation restricts the virtual space for each electron pair to the pair domains, which comprise PAOs centered close to either of the two WFs. The first-order amplitudes are obtained by solving iteratively the LMP2 equations.[12,13] Since the updates for the iterative procedure are obtained in the domain-specific orthogonal virtual basis, the singular value decomposition of the PAO overlap matrix is used to eliminate at that stage numerical redundancies among the PAOs.

As for the HF part, the most important LMP2 input parameters have been tightened. The PAOs have been constructed in the reciprocal space[15] represented by $20 \times 20 \times 20$ **k**-points. All amplitudes for WF-pairs with inter-electron distance up to 13 Å have been explicitly included in the LMP2 equations. The corresponding two-electron integrals have been calculated via the local direct-space density fitting technique[26] with mixed Poisson/Gaussian-type auxiliary basis sets, converted from the molecular aug-cc-pV5Z GTO-type fitting sets[29] according to the procedure described in Ref. 26. For the ghost centers in the bond midpoints, the aug-cc-pV5Z fitting basis of the helium atom was used. The local fit-domains, i.e., the sets of supporting centers for each of the fitted densities, were chosen to include 25 atoms.[26] The pair energies beyond 13 Å have not been evaluated explicitly, but extrapolated according to the C_6/r^6-fit and summed up.[12] The tolerance for the eigenvalues of the PAO overlap matrix in the singular value decomposition, which defines the numerical redundancy in the virtual space, was set to 10^{-4}. Since core correlation cannot be treated accurately with standard valence AO and fitting basis sets only valence electrons are correlated.

For ease of comparison to other studies,[10,16,18–21] in all our calculations we used the experimental geometry of LiH with the lattice constant of 4.084 Å.

III. RESULTS AND DISCUSSION

A. Basis set choice and convergence to the CBS limit

The full basis set specification (i.e., the list of exponents and contraction coefficients) is given in the supplementary information,[33] while here the general strategy for construction of the basis sets, and their main features are discussed. In this study, several orbital basis sets of increasing quality are employed. We start from the [4s3p2d1f]-basis set A, which

is used to generate the HF reference. The hydrogen part of this basis originates from the molecular cc-pVQZ basis set,[1] which is just slightly modified. The molecular basis set for Li contains very diffuse orbitals and is therefore inapplicable in the periodic context without substantial modification. The s- and p-shells for this atom are also taken from the cc-pVQZ basis, but with the three most diffuse components decontracted, two of them significantly upscaled and one completely removed. The d- and f-shells are taken from cc-pVTZ, but also considerably upscaled. This basis set, denoted as A, provides the HF result very close to the limit and further extensions are constructed as augmentations of this basis.

In Fig. 1, we plot the LMP2 valence correlation energies obtained with different basis sets and also the reference values calculated using the hierarchical method.[10,21,32] The periodic LMP2 double-zeta energy[30,31] is more than 20% above the limit, rendering such a basis as indeed too poor for correlated calculations.

Although the basis set A has been derived to a large extent from cc-pVQZ, the corresponding correlation energy is quite above the reference cc-pVQZ result, and is instead rather close to that of cc-pVTZ. The upscaling of the exponents of diffuse orbitals, which is not really harmful (on the contrary, very useful) at the HF level, seems to somewhat affect the correlated result. On the other hand, this basis set has virtually no redundancies and is, therefore, straightforwardly applicable in both HF and LMP2 calculations, which makes it a reasonable practical choice for MP2 applications. Expansions of the basis A are treated via the dual basis set technique,[15] i.e., only at the LMP2 stage. In this case, evaluation of the first-order singles with the bigger basis provides an estimate for the improvement in the HF energy. In the following, we denote the basis sets according to the components, which constitute them. All the basis sets employed here contain the basis A. The basis set extensions used only at the LMP2 stage will be enclosed in parentheses.

In the basis sets of the next level, an approximate optimization (up to the second significant digit in values of the exponents) of one s-, p-, d- and f-shell centered on Li

atom has been carried out by minimizing the LMP2 19-atom domain correlation energy. In order to speed up the basis set optimization process, we used the same exponent for s-, p- and d-orbitals. The optimized AOs turned out to be considerably less diffuse than those in the molecular cc-pVQZ basis (0.14 vs 0.02 bohr^{-2} for the s-orbitals), but more diffuse than those of the basis set A (0.21 bohr^{-2}). Inclusion of these four shells led to a noticeable lowering of the correlation energy, which started approaching the cc-pVQZ reference value.

An expansion of the basis set by adding a shell of each angular momentum (up to $l = 3$) on both atoms in the basis A(BC) (constituting thus [5s4p3d2f]H/[6s5p4d3f]Li set) allowed for a further improvement of the correlation energy, although not very large, but noticeable. For the new functions of the C-set, the exponents were not optimized but rather chosen to fill the gaps in the basis A(B). The resulting energy comes quite close to the reference cc-pVQZ value, but still remains slightly above.

In order to try to reach convergence with the atom-centered basis set size, we added another two shells in each angular momentum, one with tight functions: set D, the other with diffuse ones: set E. However, this basis set expansion gives only a marginal improvement of the results, whereas the fraction of redundant functions becomes substantial and the cost of the calculations noticeably grows (the elapsed times for A, A(BC), and A(BCDE) were 13, 36 and 76 h, respectively, in nondedicated mode). In fact, the A(BCDE) basis allowed us to reach a value just slightly below the reference cc-pVQZ result. This energy though remains approximately more than 1.3% above the extrapolated basis set limit reference value. To explain this discrepancy, we have investigated if it is possible at all to get closer to the basis set limit, when using the atom-centered basis sets without g- and higher angular momentum AOs. Test calculations on small LiH clusters using a cc-pV5Z(Li)/cc-pV6Z(H) basis set with and without AOs beyond the f-type demonstrated that the absence of these higher angular momentum functions results in an underestimation of the correlation energy by approximately 1.5%.

In order to compensate for this deficiency, we included basis functions centered on the mid-points between each pair of nearest-neighbour Li and H atoms. The point-group symmetry generates for such a site a 6-point star of ghost centers for each Li or H atom. For the AO-centered part of the basis, we have chosen A(BC) which was already close to saturation. For technical reasons, the HF calculation has been done with one tight s-type orbital per ghost center (the AF basis set). The bond-function G-part of the AF(BCG) basis consisted of one shell of each angular momentum ($l \leq 3$). The values for the exponents in the G-part were roughly optimized (up to the first digit after the decimal point), by performing 13-atom domain LMP2 calculations with the AF(BC) basis plus the particular shell to be optimized.

The use of the bond-centered functions significantly improves the results. In combination with big domains (see below), it allowed us to finally approach the reference basis set limit correlation energy (i.e., –0.04134 hartree). Nowadays, bond-centered orbitals are rarely used in molecular calculations,[34] where the application of optimized atom-
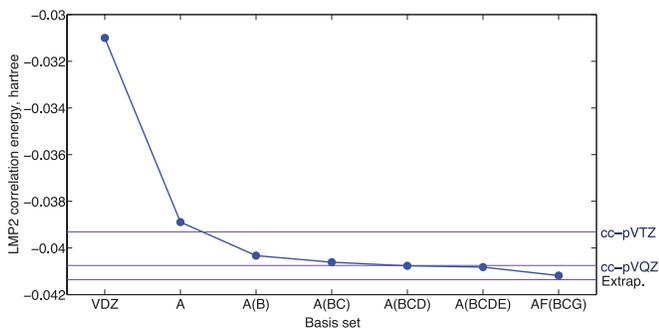

FIG. 1. The basis set dependence of the periodic LMP2 valence correlation energy for the LiH crystal in experimental geometry. LMP2 calculations have been performed with 27-atoms domains for the basis sets without the bond functions and 37-atom domains for the AF(BCG) basis. The results with the basis set of a double zeta quality, marked as VDZ, are taken from Refs. 30 and 31 and correspond to 19-atom domains. Reference energies, marked according to the basis set used as cc-pVTZ, cc-pVQZ, and Extrap., are obtained by the hierarchical method (Refs. 10, 21, and 32).

TABLE I. Convergence of the periodic LMP2 valence correlation energy with the domain size in case of A and AF(BCG) basis sets. The domains are specified by the number of the coordination spheres around the WF center (star), including ghost centers in the case of the AF(BCG) basis, the atom-type constituting each star, the domain cutoff radius (R), the number of atoms in the individual WF domains N_{AT} and the maximal number of PAOs in the pair-domains (N_{PAO}^{MAX}). The LMP2 correlation energy is denoted as E_2^{LMP2}. An estimate of the fraction of the canonical MP2 energy recovered by LMP2 (% corr.) is provided as the ratio (in percent) with respect to the largest-domain LMP2 results. For the atom-type of the bond-centers, populated with basis functions in the AF(BCG) basis set, the symbol X is used.

	Star	Atom	R(Å)	N_{AT}	N_{PAO}^{MAX}	E_2^{LMP2}, hartree	% corr.
Basis set A							
	0	H	0.	1	60	−0.033444	85.58
	1[a]	Li	2.0420	7	408	−0.038363	98.17
	2[b]	H	2.8878	19	1128	−0.038832	99.37
	3	Li	3.5368	27	1592	−0.038892	99.53
	4	H	4.0840	33	1952	−0.038946	99.66
	5	Li	4.5661	57	3344	−0.039027	99.87
	6	H	5.0019	81	4784	−0.039048	99.92
	7	H	5.7756	93	5504	−0.039051	99.93
	8	Li	6.1260	123	7186	−0.039069	99.98
	9	Li	6.4574	147	8386	−0.039077	
Basis set AF(BCG)							
	0	H	0.	1	92	−0.035664	86.26
	1	X	1.0210	7	296	−0.039653	95.91
	2[a]	Li	2.0420	13	1028	−0.041056	99.30
	3[b]	X	2.2830	37	1844	−0.041182	99.61
	4	H	2.8878	49	2948	−0.041249	99.77
	5	X	3.0630	79	3968	−0.041316	99.93
	6	Li	3.5368	87	4944	−0.041334	99.98
	7	X	3.6813	111	5760	−0.041344	

[a]The standard domain (i.e., with the default Boughton-Pulay tolerance (Ref. 35) of 0.985).
[b]The extended domain (i.e., the standard domain extended to the nearest neighbors).

centered basis sets is straightforward and efficient. However, in periodic systems, where the basis set problem has not yet found a stable and universal solution, the use of such functions becomes productive for obtaining highly accurate results. Indeed, the high-angular momentum functions, known to be important for the description of the Coulomb hole, can be substituted with lower angular momentum functions centered away from the atoms. At the same time, we note that the inclusion of bond-functions leads to a substantial increase of the computational cost (from 36 to 98 h elapsed).

B. Effect of the domain size

In order to reach full convergence to the MP2 limit, after having solved the basis set issues as just discussed, one needs to eliminate the domain error of the local approximation. Usually, this error amounts to 1−2% of the canonical correlation energy within a given basis.[25] Due to the systematic nature of this error, it to a large extent cancels out in the energy differences, but for our purposes it has to be explicitly removed. Since neither the AO-based canonical nor the full domain or explicitly correlated[36] local MP2 treatment is available in the periodic case, the only remaining option is to progressively increase the domain sizes until convergence is reached. In 3D packed systems, the size of domains usually grows fast with the number of coordination spheres of atoms included (or as R^3 where R is a domain cutoff radius).

We have performed calculations by employing domain sizes up to 147 atoms or 9 coordination spheres surrounding the WF-center for the basis set A and 111 atoms or 7 coordination spheres for the basis set AF(BCG)). In LMP2 routine calculations, one never deals with domains of this size. In case of the atom-centered basis sets, the Boughton-Pulay tolerance[35] value of 0.985, which is usually the default for domain determination,[25] corresponds to the 7-atom domain. For additional accuracy in local MP2 calculations, a further extension of domain sizes to include the next nearest neighbors is sometimes done, which then recovers more than 99% of the canonical result. In our case, this would correspond to 19-atom domain.

Table I compiles the results related to the convergence of the LMP2 correlation energy with respect to the domain size, studied for the basis sets A and AF(BCG). With the very small 1-atom domains the local approximation error is clearly large and dominant. But very soon it becomes insignificant for applications: taking the 147-atom-domain energy as the reference for the basis set A (the difference between 123- and 147-atom domain energies is within the microhartree region), the 7-atom-domain calculation captures more than 98% of the correlation energy, with 19-atom it is already 99.4% and with 57-atom nearly 99.9%. A similar pattern holds for the basis set AF(BCG), yet the convergence with respect to domain radius is quicker due to the fact that the number of functions for a given domain radius is much larger. The same effect has been observed in molecular local correla-

TABLE II. The basis set limit estimates for all-electron HF and valence MP2 correlation energies for the LiH crystal at the experimental geometry.

Code/method	Model	Basis set type	E_{HF}, hartree	E_2^{MP2}, hartree
Hierarchical method[a]	Cluster/Periodic	AO/Plane wave	−8.06472	−0.04136
VASP[b]	Periodic	Plane wave	−8.06446	(−0.04170)
CP2K[c]	Periodic	AO	−8.06454	
GAUSSIAN[c]	Periodic	AO	−8.06454	
CRYSTAL[d]	Periodic	AO	−8.06454	
CRYSTAL/CRYSCOR[e]	Periodic	AO	−8.06475	−0.04134

[a]References 10, 18, 21, and 32.
[b]Reference 16.
[c]Reference 19.
[d]Reference 20.
[e]This work.

tion calculations.[37] The stable convergence rate with domain size illustrates the robustness of the code also in case of very big domains (e.g., for 147-atom domains and basis set A the largest pair-specific virtual manifold exceeds eight thousand functions).

C. Comparison with the previous work

As was mentioned above, in the last few years several attempts to benchmark the close to the basis set limit HF and correlation energies for LiH have been done. In Table II, we provide the values for the total HF and MP2 correlation energies reported in the literature together with those obtained in the present work.

In the hierarchical method, the HF energy has been evaluated using the periodic pseudopotential approach and the pseudopotential error has then been corrected via finite cluster all-electron calculations employing AO basis sets.[18] The pure periodic approaches[16,19,20] provided rather similar results, being just a few tenths of a millihartree above the former. We note that in Ref. 16 not the total but rather the cohesive energies are reported, together with the HF energy for the Li atom. In order to estimate the value for the total HF energy in this case, we assumed the basis set limit energy for the H atom of −0.5 hartree.

In our calculations, the explicit evaluation of the HF energy with the basis AF amounted to −8.06460 hartree. Furthermore, the first-order singles contribution[15,22] evaluated with the larger basis (in our case AF(BCG)) in the dual basis set scheme (−0.00015 hartree) allowed for a further correction of the remaining basis set deficiency. In fact, it represents a perturbative estimate of the energy increment in the first HF iteration within the larger basis set, provided that the starting-guess density is the one from the converged HF in the smaller basis set (here AF).

For the MP2 correlation energy, there are only two sources of reference data. The first one was obtained via the finite cluster hierarchical method,[10,21,32] where the correlation energy was extrapolated using cc-pV[T-Q]Z basis sets. The second is from PAW/plane-wave canonical MP2 calculations.[16] In the latter again not the frozen core total energy, but rather the all-electron cohesive energy is reported. In order to compare to our result, we subtracted the value

of −0.00229 hartree, which is the core correlation contribution to the cohesive energy, evaluated in Ref. 10 using the cc-pCVTZ basis set, from the plane-wave correlation energy. This estimate is approximate, since the amount of the cohesive energy due to the core correlation in the PAW formalism might differ from that value and therefore we provide the corresponding value in parentheses.

The lowest value for the LMP2 energy, obtained in this study, namely that of the AF(BCG) basis and 111 atoms in the domain, is given in Table II. This energy as well as the HF result are in an excellent agreement with the reference values, especially those calculated within the finite cluster approach.

IV. CONCLUSIONS

In the present study, we have demonstrated that it is indeed possible to reach the basis set limit in periodic AO-based correlated calculations within the local correlation framework. Very good agreement with previous finite cluster as well as plane-wave calculations has been achieved. Despite the fact that the periodic local approach is not specifically designed for giving accurate total energies, but rather relative energies, the convergence to the canonical result through extension of local excitation domains is reached with the addition of a few coordination spheres of atoms. This demonstrates the robustness of the periodic density fitted local MP2 method as implemented in the CRYSCOR code.

A series of basis sets for solid LiH, allowing for systematic improvement of the results, has been constructed and analysed, which can serve also as a benchmark in further development of periodic correlation methods, e.g., periodic explicit-correlation or basis-set extrapolation schemes. A general strategy for choosing basis sets in AO-based periodic correlated calculations can be proposed. With the exception of molecular crystals,[38,39] the standard molecular basis sets of triple or quadruple-zeta quality are hardly directly applicable due to the presence of orbitals, which might be too diffuse for periodic HF calculations. Upscaling and/or removal of such orbitals in these basis sets could be a practical solution in order to obtain HF energies close to convergence and correlation energies of triple-zeta quality. A further expansion of the basis set is also possible via the dual basis set

technique, which can lead to a noticeable improvement of the results. The use of bond-centered functions is recommendable in cases when very high accuracy is needed, in order to circumvent the present lack of high angular momentum AOs beyond f-type.

Future work will address different ionic and covalent crystals. A generalization to the periodic case of the molecular explicitly correlated schemes, which converge more rapidly toward the basis set limit, is also under development.

[1] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).

[2] A. Halkier, T. Helgaker, P. Jorgensen, W. Klopper, H. Koch, J. Olsen, and A. Wilson, Chem. Phys. Lett. **286**, 243 (1998).

[3] W. Kutzelnigg and W. Klopper, J. Chem. Phys. **94**, 1985 (1991).

[4] W. Klopper, F. R. Manby, S. Ten-no, and E. F. Valeev, Int. Rev. Phys. Chem. **25**, 427 (2006).

[5] H.-J. Werner, T. B. Adler, and F. R. Manby, J. Chem. Phys. **126**, 164102 (2007).

[6] C. Hattig, D. P. Tew, and A. A. Köhn, J. Chem. Phys. **132**, 231102 (2010).

[7] J. G. Hill, K. A. Peterson, G. Knizia, and H.-J. Werner, J. Chem. Phys. **131**, 194105 (2009).

[8] H. Stoll, Phys. Rev. B **46**, 6700 (1992).

[9] B. Paulus, Phys. Rep. **428**, 1 (2006).

[10] S. J. Nolan, M. J. Gillan, D. Alfe, N. L. Allan, and F. R. Manby, Phys. Rev. B **80**, 165109 (2009).

[11] P. Y. Ayala, K. N. Kudin, and G. E. Scuseria, J. Chem. Phys. **115**, 9698 (2001).

[12] C. Pisani, L. Maschio, S. Casassa, M. Halo, M. Schütz, and D. Usvyat, J. Comp. Chem. **29**, 2113 (2008).

[13] L. Maschio, D. Usvyat, F. R. Manby, S. Casassa, C. Pisani, and M. Schütz, Phys. Rev. B **76**, 075101 (2007).

[14] L. Maschio and D. Usvyat, Phys. Rev. B **78**, 073102 (2008).

[15] D. Usvyat, L. Maschio, C. Pisani, and M. Schütz, Z. Phys. Chem. **224**, 441 (2010).

[16] M. Marsman, A. Grüneis, J. Paier, and G. Kresse, J. Chem. Phys. **130**, 184103 (2009).

[17] A. Grüneis, M. Marsman, and G. Kresse, J. Chem. Phys. **133**, 074107 (2010).

[18] M. J. Gillan, D. Alfe, S. de Gironcoli, and F. R. Manby, J. Comp. Chem. **29**, 2098 (2008).

[19] J. Paier, C. V. Diaconu, G. E. Scuseria, M. Guidon, J. VandeVondele, and J. Hutter, Phys. Rev. B **80**, 174114 (2009).

[20] B. Civalleri, R. Orlando, C. M. Zicovich-Wilson, C. Roetti, V. R. Saunders, C. Pisani, and R. Dovesi, Phys. Rev. B **81**, 106101 (2010).

[21] F. R. Manby, D. Alfe, and M. J. Gillan, Phys. Chem. Chem. Phys. **8**, 5178 (2006).

[22] K. Wolinski and P. Pulay, J. Chem. Phys. **118**, 9497 (2003).

[23] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, and M. Llunell, CRYSTAL09 User's Manual, Università di Torino, Torino; http://www.crystal.unito.it (2009).

[24] S. Saebø and P. Pulay, Chem. Phys. Lett. **113**, 13 (1985).

[25] M. Schütz, G. Hetzer, and H. J. Werner, J. Chem. Phys. **111**, 5691 (1999).

[26] M. Schütz, D. Usvyat, M. Lorenz, C. Pisani, L. Maschio, S. Casassa, and M. Halo, in *Accurate Condensed-Phase Quantum Chemistry*, edited by F. R. Manby (CRC Press, Taylor and Francis, New York, 2010), pp. 29–55.

[27] C. M. Zicovich-Wilson, R. Dovesi, and V. R. Saunders, J. Chem. Phys. **115**, 9708 (2001).

[28] S. Casassa, C. M. Zicovich-Wilson, and C. Pisani, Theor. Chem. Acc. **116**, 726 (2006).

[29] F. Weigend, M. Häser, H. Patzelt, and R. Ahlrichs, Chem. Phys. Lett. **294**, 143 (1998).

[30] S. Casassa, M. Halo, L. Maschio, C. Roetti, and C. Pisani, Theor. Chem. Acc. **117**, 781 (2006).

[31] M. Halo, private communication (2010).

[32] S. J. Nolan and F. R. Manby, private communication (2009).

[33] See supplementary information at http://dx.doi.org/10.1063/1.3595514 for the basis set specification.

[34] E. Jakubikova, K. Rappé, and E. Bernstein, J. Phys. Chem. A **110**, 9529 (2006).

[35] J. W. Boughton and P. Pulay, J. Comp. Chem. **14**, 736 (1993).

[36] T. B. Adler, H.-J. Werner, and F. R. Manby, J. Chem. Phys. **130**, 054106 (2009).

[37] H.-J. Werner and K. Pflüger, Annu. Rep. Comput. Chem. **2**, 53 (2006).

[38] L. Maschio, D. Usvyat, M. Schütz, and B. Civalleri, J. Chem. Phys. **132**, 134706 (2010).

[39] A. Erba, L. Maschio, S. Salustro, and S. Casassa, J. Chem. Phys. **134**, 074502 (2011).