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Comment on “Accurate Hartree-Fock energy of extended systems using large Gaussian basis sets”

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In a recent paper on Hartree-Fock (HF) calculations on solid LiH with large Gaussian-type basis sets Paier *et al.* (Phys. Rev. B **80**, 174114 (2009)) report a comment that we dispute: that similar calculations appear unlikely to be feasible using the CRYSTAL code. Here we show that using a full HF approach within periodic boundary conditions as implemented in the CRYSTAL code the same total energy is obtained as from the schemes adopted by Paier *et al.*

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Recently, solid LiH has been used as a benchmark system to establish the Hartree-Fock (HF) limit¹⁻³. In particular, Paier *et al.*³ showed that a large Gaussian-type basis set ($8s3p2d1f/6s3p2d1f$ for H and $13s6p2d1f/11s5p2d1f$ for Li) can be used to arrive close to such a limit.

Two different schemes have been adopted for obtaining the HF energy:

(i) Thirty-one short-range screened-exchange Hartree-Fock calculations are performed with decreasing screening parameter ω . The results are fitted and extrapolated to $\omega=0$, corresponding to the unscreened (full-range) HF exchange.

(ii) A truncated Coulomb operator, large supercells and the single Γ point in reciprocal space are the ingredients of the second approach; a supercell of the conventional cell as large as $5\times 5\times 5$ (containing then 1000 atoms) has been used, with a difference of $40 \mu E_h$ (per LiH couple) in total energy with respect to the smaller (and then less accurate) calculation with the $4\times 4\times 4$ supercell.

The HF energies obtained through the two schemes are very similar (-8.064543 and $-8.064545 E_h$, respectively).

In the discussion of their results, the authors claim that: (i) a full HF calculation on solid LiH using such large Gaussian basis sets has not been published, yet, and (ii) that calculations “appear unlikely to be feasible using the current CRYSTAL code” that implements a full HF scheme. A similar issue was also recently raised by other authors¹.

Here we show that with the current CRYSTAL version (i.e. CRYSTAL06⁴) and employing the same basis set as Paier *et al.*^{3,5}, with a single run (and then without any extrapolation scheme or supercell calculation), by properly setting up all computational parameters, the same total energy can be reached at a relatively low cost. Results are reported in Table I.

The use of large basis sets requires severe computational conditions to be adopted in CRYSTAL, in partic-

ular when convergence of the total energy to $10^{-6} E_h$ is targeted. The most relevant thresholds are (see refs. 4 and 6 for an explicit definition of the general strategy and numerical data): (i) the ones controlling the truncation of the Coulomb and exchange series (TI in the Table I); (ii) the ones controlling the use of a multipolar expansion for four-center integrals (ME); (iii) the one defining the k -point sampling of the Brillouin Zone (IS). The dependence of HF total energy from these parameters is documented in Table I. Calculations have been performed at the experimental lattice constant, $a=4.084 \text{ \AA}$. Convergence with respect to ME (M-O rows) and IS (P-R rows) is very rapid; the same is true for the Coulomb tolerances (TI1 and TI2), and the exchange tolerance truncating the overlap among product Gaussians (TI3), as shown by cases H to L. As expected, convergence for the other exchange series parameters (TI4 and TI5) is slower. Cases A-G show however that the maximum difference of the “converged” total energy from the loosest case (case A, for which TI4=15, TI5=30) is smaller than $2 \cdot 10^{-5} E_h$, and reduces by an order of magnitude beyond TI4=20 and TI5=80.

Results are then numerically quite stable and very close to the values reported in ref. 3. The error bar resulting from the table is well within (or much smaller than) the $50\mu E_h$ estimated by Paier *et al.*³ for the total energy resulting from their calculations.

For the calculation of the HF cohesive energy of solid LiH we refer to the HF limit for the atomic energies of H ($-0.5 E_h$) and Li ($-7.432727 E_h$). Results in Table I are almost independent from the computational conditions and around $-131.81 mE_h$. If the atomic energies are computed with the current basis set by surrounding H and Li atoms with ghost atoms (92 and 170, respectively) the values $-0.499974 E_h$ and $-7.432595 E_h$ are obtained for H and Li, respectively, in accord with those reported by Paier *et al.*³ With these references, a cohesive energy of $-131.98 mE_h$ is obtained, in excellent agreement (better

than $0.1 mE_h$) with the best estimate obtained by Gillan et al.¹ of $-131.95 mE_h$.

By using the same computational parameters as case F of Table I, we also computed the HF equilibrium lattice parameter and bulk modulus of solid LiH to be 4.105 Å and 32.90 GPa. Again, this result is in nice accord with the value reported by Paier et al.³ (i.e. $a=4.105$ Å and $B=32.34$ GPa) for the first of the two schemes they adopted.

Truncation criteria are also important in determining the cost of the calculation. It is worth noting that space group symmetry is fully exploited in our approach, both in direct and reciprocal space. The last column shows that the CPU time (on a single processor) never exceeds 30 minutes, and the results are already very accurate at a cost of about 10 minutes.

The target in the present calculations is reached with a very limited computational effort and with the standard code available at the CRYSTAL web site for cross-check. Only case A can be run with the present *public* version of CRYSTAL06, because one of the static dimensions of the code (defining a list of lattice vectors, and fixed long time ago when smaller basis sets and looser computational conditions could be used) is insufficient for the other cases. This limit has been removed in the new version of the code (CRYSTAL09). A “demo” version of the code is available⁷, that permits to run all cases; it can be downloaded for free and contains all the functionalities of the distributed code, the only

constraint being the number of atoms in the unit cell, limited to four. A sample input deck is also available⁸ to repeat the present calculations.

In conclusion, we demonstrated that the full HF approach as implemented in the CRYSTAL code can be used with a large basis set to obtain total energies close to the HF limit.

Comparing the accuracy of different approaches, as proposed by Paier et al., is certainly a stimulating issue, important for developers and users. A number of aspects could be considered for this purpose, concerning the use of the HF exchange (in a full HF scheme, or as an ingredient in hybrid functionals) in conjunction to high quality basis sets: (i) the accurate estimate of other properties than energy (vibrational spectra, X-ray structure factors, Compton profiles, elastic and dielectric tensors...); (ii) the applicability to more complex systems (e.g. urea bulk, α -quartz,...); (iii) the availability of the HF solution in a form suitable for a post-HF treatment of electron correlation⁹. The computational cost is in all cases an important variable to be provided and verifiable. Work is in progress and will be presented in a forthcoming paper which extends the present analysis to other periodic systems and to other properties than just energy, to show that results close to the HF limit can be obtained with reasonable effort using large Gaussian basis sets and well calibrated computational parameters.

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⁵ The exponent of one of the p shells of the basis set for lithium in ref. 3 is 0.15709110E+01 instead of 0.15709110. J. VandeVondele, private communication.

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⁷ www.crystal.unito.it/demo.html.

⁸ www.crystal.unito.it/supplement/lih/input.html.

⁹ C. Pisani, L. Maschio, S. Casassa, M. Halo, M. Schütz, and D. Usyat, *J. Comp. Chem.* **29**, 2113 (2008).

TABLE I: HF total and cohesive energy of solid LiH as a function of the computational parameters. Calculations performed with CRYSTAL06 at the experimental geometry ($a=4.084$ Å) by employing the basis set proposed by Paier *et al.*^{3,5}

Case	TI ^a	ME ^b	IS ^c	TE ^d	CE ^e	CPU Time ^f
A	6 6 6 15 30	28 (20)	12 (72)	-8.064542	-131.81	206 (16)
B	7 7 7 15 30	28 (20)	12 (72)	-8.064525	-131.80	294 (21)
C	7 7 7 15 50	28 (20)	12 (72)	-8.064525	-131.80	339 (26)
D	7 7 7 18 65	28 (20)	12 (72)	-8.064534	-131.81	483 (37)
E	7 7 7 20 80	28 (20)	12 (72)	-8.064541	-131.81	603 (46)
F	7 7 7 25 100	28 (20)	12 (72)	-8.064544	-131.82	876 (67)
G	7 7 7 30 120	28 (20)	12 (72)	-8.064546	-131.82	1226 (94)
H	6 6 6 25 100	28 (20)	12 (72)	-8.064561	-131.83	658 (51)
I	7 7 7 25 100	28 (20)	12 (72)	-8.064544	-131.82	876 (67)
J	8 8 8 25 100	28 (20)	12 (72)	-8.064544	-131.82	1127 (87)
K	9 9 9 25 100	28 (20)	12 (72)	-8.064540	-131.81	1372 (106)
L	10 10 10 25 100	28 (20)	12 (72)	-8.064539	-131.81	1763 (136)
M	7 7 7 25 100	14 (10)	12 (72)	-8.064532	-131.80	829 (64)
N	7 7 7 25 100	28 (20)	12 (72)	-8.064544	-131.82	876 (67)
O	7 7 7 25 100	100 (100)	12 (72)	-8.064544	-131.82	1144 (88)
P	7 7 7 25 100	28 (20)	12 (72)	-8.064544	-131.82	876 (67)
Q	7 7 7 25 100	28 (20)	10 (47)	-8.064544	-131.82	863 (66)
R	7 7 7 25 100	28 (20)	8 (29)	-8.064544	-131.82	860 (66)

^a Tolerances for one- and two-electron integrals calculation:

TI1, TI2 concern the truncation of the Coulomb series; TI3, TI4 and TI5 that of the exchange series

^b Multipolar expansion: Coulomb (exchange) tolerances

^c Shrinking factor and, in parentheses, number of \mathbf{k} -points, for the sampling of the irreducible Brillouin zone

^d Total energy in E_h

^e Cohesive energy in mE_h referred to atomic energies at the HF limit

^f Time in seconds on a single core Intel Xeon E5440 2.33 GHz with 2GB RAM (DDR2 667MHz) HD 250GB SATAII 7200 rpm (16MB cache) in a conventional SCF scheme. Executables compiled with Intel FC 11.1 for EMT64 processors. TE converged on the seventh decimal figure (CPU time per each SCF cycle in parentheses).