Density Functional Theory Study of the Structural Properties of 

PuH$_x$, 2 $\leq x \leq$ 3 

Sven P. Rudin 

Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA 

(Dated: May 11, 2014) 

Abstract 

Plutonium dihydride and trihydride show strikingly similar crystal structures when viewed as close-packed Pu planes with ABC and AB stacking, respectively. The similarity serves as a framework for density functional theory (DFT) calculations of PuH$_2$, PuH$_3$, and intermediate compositions. Agreement between structures observed in experiment and in the DFT description of the Pu-H system requires accounting for the strong electronic correlation in the $f$ orbitals, achieved here with the addition of a Hubbard parameter $U$. The hysteresis measured between hydriding and dehydriding can be attributed to the effect of stacking of the close-packed Pu planes on the energy as a function of stoichiometry, calculated using the GGA+U approach. Changes in the interstitial positions occupied by the H atoms affect the energy by amounts that are negligible compared to room temperature; changes in the magnetic structure lead to equally small energy differences. 

PACS numbers: 71.27.+a, 71.10.Fd, 61.72.jj
I. INTRODUCTION

The safe storage of plutonium will require a better understanding of the metal’s corrosion. Hydrogen-catalyzed corrosion is of greatest concern, given that plutonium hydride in particular not only forms easily, but is also highly reactive. Yet the solid Pu-H system has not received much theoretical study, and such studies have focused on the two stoichiometric compounds, with limited attempts to connect them with intermediate compositions. Experimentally much more has been done.

Known Pu-H system stoichiometries range from the pure metal through the dihydride to the trihydride. Hydrogen shows solubility in Pu for up to 1-2 at. % H. Adding additional H into the system leads to a region wherein the Pu metal and the dihydride coexist, the upper limit is a temperature-dependent PuH$_x$ stoichiometry with $x = 1.75 - 1.88$. Here a second region of H solubility appears, now in PuH$_2$. The upper limit of this region, PuH$_{2.75}$, marks the beginning of a region of coexistence between the dihydride and the trihydride.

This phase transition connecting di- and trihydride shows a large hysteresis effect between cycles of hydriding and dehydriding. The transformation proceeds more easily for dehydriding than for hydriding with the largest difference in the H pressure (a factor of 10$^4$) near $x = 2.9$. Experimentally, the hysteresis appears to have structural origins.

The current work explores the structures of the di- and trihydride in terms of how they relate to each other and how they change for intermediate stoichiometries. Section II reveals remarkable similarities between the di- and trihydride crystal structures. The ensuing sections use the similarities to construct a framework and describe calculations aimed at understanding the hysteresis.

II. CRYSTAL STRUCTURE SIMILARITIES

While the di- and trihydride crystal structures have very different symmetries, their Pu sublattices can both be viewed as close-packed lattices. The cubic PuH$_2$ appears in the fluorite structure (Fig. 1(a)); the hexagonal PuH$_3$ is isostructural to Na$_3$As (Fig. 1(b)). The Pu sublattice of PuH$_2$ corresponds to a face-centered cubic (fcc) crystal structure, making it close-packed layers with ABC stacking. The Pu sublattice of PuH$_3$ takes on a hexagonal close-packed (hcp) crystal structure, making it close-packed layers with AB stacking. These
FIG. 1. (Color online) Monoclinic structural units (dark red edges) of (a) PuH$_2$ and (b) PuH$_3$ as they relate to the conventional unit cells (grey edges). Large spheres represent Pu atom sites, small spheres represent H atom sites; edges of the octahedra formed by Pu sites appear as thin lines. The lattice of PuH$_2$ repeats a monoclinic structural unit (MSU), while that of PuH$_3$ repeats a MSU and its mirror image. The top view (with c edge into the page) of the MSUs for (c) PuH$_2$ and (d) PuH$_3$ emphasizes the similarity between the two systems: identical Pu positions within the MSUs, and H positions within the MSUs that differ almost only in the additional H atoms in the faces spanned by b and c for PuH$_3$ (the close-packed planes).

structures echo the layered, close-packed nature already apparent in crystal structures of pure Pu: the face-centered cubic structure of the Pu sublattice of PuH$_2$ is that of δ-Pu, and the AB stacking of Pu sublattice of PuH$_3$ can be related to the α-Pu structure’s repeating two planes of a distorted hexagonal structure.$^{10}$

The di- and trihydride crystal structures have very different primitive unit cells but can also be constructed from structural units with surprisingly comparable dimensions and internal structure. These are monoclinic structural units (MSUs). Figure 1 shows a description of (a) the PuH$_2$ lattice in terms of repeated MSUs and (b) the PuH$_3$ lattice built from a similar MSU and its exact mirror image. Each MSU shifts the Pu positions from one plane to the next, in ABC stacking the shift simply repeats, whereas in AB stacking the direction of the shift alternates.

Table II shows the close proximity of the experimental dimensions of the monoclinic structural units for PuH$_2$ and PuH$_3$. The experimental Pu-Pu distances within the planes are
| crystal   | method                  | \(a\)  | \(b\)  | \(c\)  | \(\gamma\) | \(V\)  |
|----------|-------------------------|--------|--------|--------|------------|-------|
| PuH\(_2\) ABC | experimental            | 3.79   | 6.56   | 3.79   | 55°        | 77.0  |
| PuH\(_2\) ABC | GGA, AFM                | 3.78   | 6.57   | 3.72   | 54°        | 74.5  |
| PuH\(_2\) ABC | GGA with SOC, AFM       | 3.77   | 6.54   | 3.72   | 54°        | 74.2  |
| PuH\(_2\) ABC | GGA+U, AFM              | 3.84   | 6.67   | 3.82   | 54°        | 79.5  |
| PuH\(_2\) AB  | GGA, AFM                | 3.38   | 6.90   | 3.34   | 60°        | 67.5  |
| PuH\(_2\) AB  | GGA with SOC, AFM       | 3.43   | 6.87   | 3.31   | 60°        | 67.4  |
| PuH\(_2\) AB  | GGA+U, FM               | 3.61   | 6.95   | 3.77   | 56°        | 78.5  |
| PuH\(_3\) AB  | experimental            | 4.02   | 6.55   | 3.78   | 57°        | 83.6  |
| PuH\(_3\) AB  | GGA, FM                 | 3.96   | 6.45   | 3.72   | 57°        | 79.9  |
| PuH\(_3\) AB  | GGA with SOC, FM        | 3.95   | 6.45   | 3.71   | 57°        | 79.3  |
| PuH\(_3\) AB  | GGA+U, FM               | 4.07   | 6.61   | 3.82   | 57°        | 86.2  |
| PuH\(_3\) ABC | GGA, FM                 | 3.70   | 6.41   | 3.70   | 55°        | 71.6  |
| PuH\(_3\) ABC | GGA with SOC, FM        | 3.68   | 6.44   | 3.69   | 55°        | 71.7  |
| PuH\(_3\) ABC | GGA+U, AFM              | 3.71   | 6.80   | 3.70   | 56°        | 77.5  |

TABLE I. Measured and calculated dimensions of monoclinic structural units in PuH\(_2\) and PuH\(_3\). Lattice parameters \(a\), \(b\), and \(c\) are given in Å, volume \(V\) in Å\(^3\). The angle \(\gamma\) describes the slant of the MSUs (see Fig. 1) and is not related to the hexagonal nature found in the close-packed Pu layers. Results are reported for magnetic structure with the lowest energy for the particular stoichiometry, lattice structure, and method. All GGA+U calculations employ \(U = 4\) eV.

nearly identical for PuH\(_2\) and PuH\(_3\), as evidenced by the in-plane lattice vectors \(b\) and \(c\), which differ between the structures by only 0.01 Å. The angle \(\gamma\) also differs by only two degrees between structures. The single large difference appears for \(a\): the spacing between layers is 6% larger for PuH\(_3\) to accommodate the additional H atoms.

The internal structure of the MSUs for PuH\(_2\) and PuH\(_3\) also appear remarkably similar. The Pu sites are identical. The H atoms in PuH\(_2\) sit at the centers of tetrahedra formed by Pu atoms. These tetrahedral interstices appear in planes located at \(\frac{3}{4}b\) and \(\frac{2}{4}b\) in the MSU of Fig. 1(c). Corresponding H atoms appear on almost unchanged sites within the MSU of PuH\(_3\) (on the 4f Wyckoff positions) and are joined by H atoms on the faces spanned by \(b\) and \(c\) (2b positions). Within the primitive unit cell of PuH\(_3\) these two types of H sites also
have different environments, the former still sit in Pu tetrahedra, albeit slightly deformed, the latter sit at the centers of equilateral Pu triangles.

III. CALCULATION METHOD

The similar MSUs of Pu di- and trihydride provide a framework within which intermediate compositions can be explored computationally. The calculations presented here are limited to unit cells with four Pu sites and between eight and twelve H atoms. Initial unit cells correspond to the two MSUs shown in Fig. 1(a) and in Fig. 1(b) (where the chevron shape is made into an actual unit cell) with added and removed H atoms, respectively. These initial configurations often relax surprisingly slow with false plateaus, which require rather small convergence criteria to overcome (see below). These unit cells limit the current study to structures with AB and ABC stacking. A systematic study of whether the Pu hydrides favor other stacking sequences will likely shed more light on the system but also require significantly more computational effort.

The calculations discussed here neglect thermal effects. Contributions to the free energy from the phonons in particular are important, given the small mass of the H atoms. The current results do reveal many small energy differences between magnetic states and various configurations of the H atoms, which even the zero-point energy will affect. However, in addition to being beyond the scope of this work, the calculation of phonons and including their thermal effects will not likely overcome the inaccuracy inherent in the density functional theory (DFT) method. Connections made between the results and experimental data do involve thermal effects in the form of comparisons with the energy scale set by room temperature, but the main conclusions involve large enough energy differences to be immune to neglected contributions from the phonons.

The results presented here originate in DFT calculations using the VASP package. The calculations make use of the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof. The Pu(5f, 6d, 7s) and H(1s) electrons are treated in the valence with projector-augmented wave potentials. The calculations employ the linear tetrahedron method with Blöchl corrections, a k-point mesh of density 60 Å\(^{-1}\), and an energy cutoff of 500 eV. The self-consistent cycles are converged to within 10\(^{-5}\) meV to enable the 10\(^{-4}\) meV ionic stopping criteria needed to overcome the false plateaus mentioned above. The calcu-
lations allow spin polarization and compare two types of magnetic structure, ferromagnetic (FM) and antiferromagnetic (AFM).

Because DFT in the GGA fails to describe PuH$_3$ as a semiconductor, the effects of including either strong electron correlation and spin-orbit coupling are investigated. Some results reported here stem from calculations that treat the on-site Coulomb repulsion between 5$f$ electrons with a Hubbard parameter $U$ (GGA+U) in the rotationally invariant form of Dudarev et al.$^{22}$ In this form the Hubbard parameter $U$ and the exchange parameter $J$ appear only in the difference $U - J$, throughout this report the difference is simply referred to as $U$. A single value for $U$ (4 eV) for all stoichiometries allows a comparison of the calculated energies and the evaluation of formation energies. While Ai et al. suggest spin-orbit coupling (SOC) can be neglected, the results presented here show some energy differences small enough for SOC to matter.

IV. RESULTS FOR PUH$_2$ AND PUH$_3$

A. DFT in the GGA

For both stoichiometric compounds, DFT in the GGA without SOC fails to deliver the correct ground state crystal structure. Curiously, the GGA would have the two hydrides switch the stacking of Pu sublattices (see Fig. 2): DFT in the GGA would have PuH$_3$ take on a cubic symmetry, i.e., ABC stacking of the Pu sublattice with H atoms at both the tetragonal and the octahedral sites; an energy difference of 110 meV per formula unit (meV/f.u.) appears relative to the experimental structure (both structures favor FM). Similarly, DFT in the GGA would have PuH$_2$ with an AB stacking of the Pu sublattice with H atoms sitting in the slightly deformed Pu tetrahedra (the Pu sublattice does not quite have hexagonal symmetry); an energy difference of 8 meV/f.u. appears relative to the experimental structure (both structures favor AFM). The value 8 meV/f.u. presents an example of an energy difference that thermal energy stemming from the phonons could strongly affect.

B. including spin-orbit coupling

DFT in the GGA with SOC shows the correct ground state crystal structure for PuH$_2$ but still fails for PuH$_3$. The correct ABC stacking for PuH$_2$ lies 41 meV/f.u. lower than
AB stacking and favors AFM over FM by 61 meV/f.u. PuH$_2$ remains a metal. For PuH$_3$, the erroneous ABC stacking lies 75 meV/f.u. lower than the correct AB stacking, and FM remains favored over AFM by 62 meV/f.u.

C. including a Hubbard U

Accounting for the electronic correlation in the $f$ orbitals describes the structures of the stoichiometric compounds in agreement with experiment. As shown by Ai et al., inclusion of the Hubbard $U$ in the calculations leaves PuH$_2$ metallic with $f$ states at and below $E_F$, while in PuH$_3$ the Hubbard $U$ opens a gap between occupied and unoccupied $f$ states. This approach (performed here without SOC) also results in the correct structures for both stoichiometric compounds: for PuH$_2$, GGA+U calculations favor the correct ABC stacking over the erroneous AB stacking by 360 meV/f.u.; for PuH$_3$, GGA+U calculations favor the correct AB stacking over the erroneous ABC stacking by 140 meV/f.u.

In both stoichiometries, the GGA+U calculations give lower energies for AFM than FM.
order. The energy differences are quite small, 60 meV/f.u. for PuH$_2$ and 20 meV/f.u. for PuH$_3$. These small values suggest a delicate balance between magnetic structures (which could easily be upset by either thermal effects or other theoretical methods). FM order appears in most experimental measurements PuH$_{2+}$ and PuH$_3$, though earlier measurements suggest AFM order for PuH$_2$. V.

RESULTS FOR PUH$_x$ WITH $2 < x < 3$

Expanding on the results for the di- and trihydride, the methods described above are applied to structures with AB and ABC stacking for PuH$_x$ with $2 < x < 3$. Systems with intermediate stoichiometries originate in PuH$_2$ and PuH$_3$ unit cells (with four Pu atoms) with added and removed H atoms, respectively. Structural optimization of these initial structures proceeds until the total energy between optimization steps differs by less than $10^{-4}$ meV; this process frequently involves unusually numerous optimization steps. Seeding with all reasonably different H placements leads to multiple (meta)stable arrangements for each stoichiometry.

Figure 3 shows the calculated formation energies (relative to the stoichiometric compounds) of PuH$_x$ structures with $2 < x < 3$. The formation energies for PuH$_x$ structures relative to PuH$_2$ and PuH$_3$ derive from comparing to the linearly-weighted energies of the di- and trihydride (i.e., to $E$(PuH$_2$) + $(x - 2)[E$(PuH$_3$) − $E$(PuH$_2$)]). The energies at these endpoints are for the most favored crystal and magnetic structure of the method in question, as outlined in the figure caption.

Structures with ABC stacking have lower energies than those with AB stacking, independent of method, with two exceptions. (1) DFT in the GGA (without SOC) fails to reproduce the correct crystal structure for PuH$_2$; (2) in the GGA+U approach, DFT reproduces the correct crystal structure for PuH$_3$. This second exception makes only the GGA+U results relevant for comparisons with experiment; consequently the remainder of this section discusses only GGA+U results. Interpolating the GGA+U results between the considered stoichiometries suggests a region of stability for ABC stacking between PuH$_2$ and just above PuH$_{2.75}$, followed by a region of stability for AB stacking starting slightly beyond PuH$_{2.75}$.

The GGA+U calculated formation energies from PuH$_2$ to PuH$_{2.75}$ remain below room temperature without changing crystal structure. This calculated thermally-accessible region
FIG. 3. (color online) Relative calculated potential energies (with respect to PuH$_2$ and PuH$_3$) of the most stable PuH$_x$ supercells with ABC stacking (squares) and AB stacking (diamonds). Energies are given relative to the most favorable crystal structure and magnetic structure of the di- and trihydride within each method: (a) AFM PuH$_2$ with AB stacking and FM PuH$_3$ with ABC stacking for GGA, (b) AFM PuH$_2$ with ABC stacking and FM PuH$_3$ with ABC stacking for GGA with SOC, (c) AFM PuH$_2$ with ABC stacking and AFM PuH$_3$ with AB stacking for GGA+U.

fits the experimentally observed region of H solubility in PuH$_2$, for which PuH$_{2.75}$ demarcates the upper limit. While these calculations reveal nothing about the kinetics of moving hydrogen into the PuH$_2$ crystal, they do suggest that, at room temperature, thermal effects will not push the hydrogen back out.

The location of H atoms in the PuH$_x$ lattice suggested by the current calculations agrees with experiment. The calculated lowest energy for PuH$_{2.25}$, PuH$_{2.5}$, and PuH$_{2.75}$ appears for structures with the additional one, two, or three H atom(s) in octahedral interstitials. Occupying additional octahedral interstitial sites (by creating tetrahedral vacancies) raises the calculated energies by between 5 and 25 meV/atom. This range of energy is easily attained at room temperature. Finite temperature also affects the free energy by way of configurational entropy, which will favor partial occupancy of both tetrahedral and octahedral sites. Tetrahedral vacancies in concert with partial occupancy of octahedral sites for
PuH$_2$ have been observed experimentally. This partial occupancy for both types of sites is also observed for PuD$_2$, for which the calculated results presented here hold equally well.

The magnetic structures found to be most favorable by the current calculations do not agree with experiment, but energy differences are small. The GGA+U calculations prefer an AFM structure for all stoichiometries. Magnetic susceptibility measurements show FM behavior for a wide range of stoichiometries, though earlier measurements suggest AFM ordering for the dihydride. The calculated energy differences between AFM and FM ordering, however, range from 5 meV/atom for PuH$_3$ to 15 meV/atom for PuH$_2$ (i.e., again an energy range easily attained at room temperature).

VI. RELATING THE GGA+U RESULTS TO THE HYSTERESIS

The small energy difference between AB and ABC stacking for PuH$_{2.75}$ in the GGA+U calculations warrants considering transformations between the two crystal structures near this stoichiometry. Exploratory calculations, mentioned here in passing, take the unit cell with AB stacking, shear it stepwise and relax internal coordinates until the stacking is ABC; these calculations suggest an energy barrier for this transformation comparable to room temperature. An accurate evaluation of the barrier height would require a nudged elastic band calculation that optimizes internal and unit cell degrees of freedom. This evaluation would have to be repeated for other pathways, including those in other systems with, for example, larger unit cells to accommodate alternate stacking sequences. Such calculations would go beyond the scope of this work, and furthermore would not represent macroscopic processes: in a solid of measurable size, such a concerted mechanism cannot be thermally activated.

The transformation more likely involves a locally nucleated process followed by energetically-favored growth of the transformed region, a conversion process which the current GGA+U results support. The GGA+U calculated energy differences between AB and ABC stacking at stoichiometries away from PuH$_{2.75}$ can encourage growth of a region of one type of stacking nucleated within the other type. While the values of the necessary energy differences are unknown, they are finite, which introduces a difference in the stoichiometries that foster the two transformations. This difference in stoichiometries which drive AB$\rightarrow$ABC and
ABC→AB transformations is the source of the hysteresis measured between hydriding and dehydriding.

VII. SUMMARY

Plutonium dihydride and trihydride show strikingly similar crystal structure aspects when viewed as close-packed Pu planes with ABC and AB stacking, respectively, with interstitial H atoms. The dimensions within the planes differ by only 0.01 Å, the planes are spaced 6% farther apart in PuH$_3$ compared to PuH$_2$. The H atoms situated between planes sit at almost identical positions, the additional H atoms in PuH$_3$ sit in the close-packed Pu planes. Density functional theory (DFT) calculations in the generalized gradient approximation (GGA) give structural dimensions in good agreement with experiment. For the DFT calculations to favor the stacking observed in experiment requires some treatment of the electron correlation between 5$f$ electrons, exemplified here by the GGA+U method.

The close-packed Pu planes with ABC and AB stacking interspersed with H atoms provides a framework to explore intermediate stoichiometries. The experimentally observed hysteresis, attributed to structural origins, can be explained based on the stoichiometric dependence of which type of stacking has a lower calculated energy (using the GGA+U approach). The calculated stoichiometry PuH$_x$ at which the preference switches from ABC stacking to AB stacking, slightly above $x = 2.75$, agrees well with the lower limit of the region in which experiment observes the two types of crystal structures coexisting.

Overall, the DFT calculations on the Pu-H system reveal very small energy differences (relative to room temperature) for multiple changes to the system: the AFM solutions lie below the FM solutions by small energies, changing the arrangements of the H atoms on tetrahedral and octahedral sites leads to small changes in the energy, and even changing the stoichiometry itself affects the formation energy by small amounts.

ACKNOWLEDGMENTS

This research was supported by the Los Alamos National Laboratory, under the auspices of the National Nuclear Security Agency, by the U.S. Department of Energy under Grant No.
ldrd-dr 20110011 (“Hydrogen Effects in δ-Stabilized Pu Alloys”). Many thanks go to Eric Chisolm, Scott Richmond, Dan Schwartz, Dan Sheppard, Chris Taylor, Steve Valone, and Art Voter for helpful and encouraging discussions. The author expresses a deep gratitude to Neil Henson for assistance with the ANDULU computational facility. Last, but not least, fond thanks go to Lucia Liên and Anna Lan for spurring alternative approaches to understanding.

1. J. Martz and A. Schwartz, JOM Journal of the Minerals, Metals and Materials Society 55, 19 (2003).
2. S. Richmond, J. S. Bridgewater, J. W. Ward, and T. H. Allen, IOP Conference Series: Materials Science and Engineering 9, 012036 (2010).
3. J. M. Haschke, “Synthesis of lanthanide and actinide compounds,” (Kluwer, Dordrecht, 1991) p. 1.
4. J. M. Haschke and T. H. Allen, Journal of Alloys and Compounds 320, 58 (2001).
5. O. Eriksson, Y. G. Hao, B. R. Cooper, G. W. Fernando, L. E. Cox, J. W. Ward, and A. M. Boring, Phys. Rev. B 43, 4590 (1991).
6. J. Ai, T. Liu, T. Gao, and B. Ao, Computational Materials Science 51, 127 (2012).
7. B. Ao, X. Wang, P. Shi, P. Chen, X. Ye, X. Lai, and T. Gao, Journal of Nuclear Materials 424, 183 (2012).
8. A. Bing-Yun, A. Juan-Juan, G. Tao, W. Xiao-Lin, S. Peng, C. Pi-Heng, and Y. Xiao-Qiu, Chinese Physics Letters 29, 017102 (2012).
9. R. N. R. Mulford and G. E. Sturdy, Journal of the American Chemical Society 77, 3449 (1955).
10. R. N. R. Mulford and G. E. Sturdy, Journal of the American Chemical Society 78, 3897 (1956).
11. A. T. Aldred, G. Cinadar, D. J. Lam, and L. W. Weber, Phys. Rev. B 19, 300 (1979).
12. J. W. Ward, Journal of the Less Common Metals 93, 279 (1983).
13. J. Willis, J. Ward, J. Smith, S. Kosiewicz, J. Haschke, and A. H. III, Physica B+C 130, 527 (1985).
14. J. M. Haschke, A. E. H. III, and R. L. Lucas, Journal of the Less Common Metals 133, 155 (1987).
15. G. W. McGillivray, I. M. Findlay, R. M. Harker, and I. D. Trask, AIP Conference Proceedings 673, 167 (2003).
16 A. Crocker, Journal of Nuclear Materials 41, 167 (1971).

17 G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).

18 G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).

19 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

20 P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).

21 P. E. Blöchl, O. Jepsen, and O. K. Andersen, Phys. Rev. B 49, 16223 (1994).

22 S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).

23 W. Bartscher, A. Boeuf, R. Caciuffo, J. Fournier, J. Haschke, L. Manes, J. Rebizant, F. Rustichelli, and J. Ward, Solid State Communications 52, 619 (1984).

24 W. Bartscher, A. Boeuf, R. Caciuffo, J. Fournier, W. Kuhs, J. Rebizant, and F. Rustichelli, Solid State Communications 53, 423 (1985).

25 D. Sheppard, P. Xiao, W. Chemelewski, D. D. Johnson, and G. Henkelman, The Journal of Chemical Physics 136, 074103 (2012).