Van der Waals Interactions in Density Functional Theory by combining the Quantum Harmonic Oscillator-model with Localized Wannier Functions

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Abstract

We present a new scheme to include the van der Waals (vdW) interactions in approximated Density Functional Theory (DFT) by combining the Quantum Harmonic Oscillator model with the Maximally Localized Wannier Function technique. With respect to the recently developed DFT/vdW-WF2 method, also based on Wannier Functions, the new approach is more general, being no longer restricted to the case of well separated interacting fragments. Moreover, it includes higher than pairwise energy contributions, coming from the dipole–dipole coupling among quantum oscillators. The method is successfully applied to the popular S22 molecular database, and also to extended systems, namely graphite and H$_2$ adsorbed on the Cu(111) metal surface (in this case metal screening effects are taken into account). The results are also compared with those obtained by other vdW-corrected DFT schemes.
I. INTRODUCTION

Density Functional Theory (DFT) is a well-established computational approach to study the structural and electronic properties of condensed matter systems from first principles. Although current, approximated density functionals allow a quantitative description at much lower computational cost than other first principles methods, they fail to properly describe dispersion interactions. Dispersion forces originate from correlated charge oscillations in separate fragments of matter and the most important component is represented by the $R^{-6}$ van der Waals (vdW) interaction, originating from correlated instantaneous dipole fluctuations. This kind of interactions play a fundamental role in determining the structure, stability, and function of a wide variety of systems, including molecules, clusters, proteins, nanostructured materials, molecular solids and liquids, and in adsorption processes of fragments weakly interacting with a substrate ("physisorbed").

In the last few years a variety of practical methods have been proposed to make DFT calculations able to accurately describe vdW effects (for a recent review, see, for instance, refs. 3–5). In these respect, a family of such methods, all based on the Maximally Localized Wannier Functions (MLWFs), has been developed, namely the original DFT/vdW-WF, DFT/vdW-WF2 (based on the London expression and taking into account the intrafragment overlap of the MLWFs), and DFT/vdW-WF2s (including metal-screening corrections), successfully applied to a variety of systems: small molecules, water clusters, graphite and graphene, water layers interacting with graphite, interfacial water on semiconducting substrates, hydrogenated carbon nanotubes, molecular solids, the interaction of rare gases and small molecules with metal surfaces,...

All these methods rely on the possibility of attributing the MLWFs to well separated fragments. Although this requirement is certainly satisfied in many interesting cases (interaction between saturated molecules, adsorption of rare gases on metal substrates,...), nonetheless it represents both a fundamental limitation and a practical technical complication, since the different fragments must be somehow identified.

In the present paper we overcome the above limitation by presenting a method, also based on the MLWFs, developed by adopting the coupled Quantum Harmonic Oscillator (QHO) model. This also provides an effective many body description of the long-range correlation energy, beyond a pairwise $C_6/R^6$ approximation. The new method, hereafter
referred to as DFT/vdW-QHO-WF, is successfully applied to the popular S22 benchmark set of weakly interacting molecules and also to extended systems, namely graphite and H₂ adsorbed on the Cu(111) metal surface (in this case metal screening effects are taken into account). The results are compared with those obtained by other vdW-corrected DFT schemes and with available, reference experimental values.

II. METHOD

For a system of \( N \) three-dimensional QHOs the exact total energy can be obtained\cite{10-24} by diagonalizing the \( 3N \times 3N \) matrix \( C_{QHO}^{ij} \), containing \( N^2 \) blocks \( C_{ij}^{QHO} \) of size \( 3 \times 3 \):

\[
C_{ii}^{QHO} = \omega_i^2 I; \quad C_{ij}^{QHO} = \omega_i \omega_j \sqrt{\alpha_i \alpha_j} T_{ij}
\]  

(1)

where \( I \) is the unitary matrix, and \( \omega_i \) and \( \alpha_i \) are the characteristic frequency and the static dipole polarizability, respectively, of the \( i \)-th oscillator. The interaction (correlation) energy is given by the difference between the square root of the eigenvalues \( \lambda_p \) of the coupled system of QHOs and of the eigenvalues of the uncoupled system of QHOs (namely the characteristic frequencies):

\[
E_{c,QHO} = 1/2 \sum_{p=1}^{3N} \sqrt{\lambda_p} - 3/2 \sum_{i=1}^{N} \omega_i.
\]  

(2)

The so-computed interaction energy naturally includes many body energy contributions, due to the dipole–dipole coupling among the QHOs. Moreover, it can be proved\cite{24} that, within the present model, the ACFDT-RPA (adiabatic connection fluctuation dissipation theorem-random phase approximation) correlation energy coincides with the exact binding energy \( E_{c,QHO} \). Hence, the QHO model provides an efficient description of the correlation energy for a set of localized fluctuating dipoles at an effective RPA level.

In this paper, we combine the QHO model with the MLWF technique by assuming that each MLWF can be represented by a three-dimensional harmonic oscillator, so that the systems is described as an assembly of fluctuating dipoles. Following ref.\cite{24} the bare Coulomb potential is modified to account for orbital overlap at short distances (thus introducing a short-range damping):
where \( r_{ij} \) is the distance between the \( i \)-th and the \( j \)-th Wannier Function Center (WFC), and \( \sigma_{ij} \) is an effective width, \( \sigma_{ij} = \sqrt{S_i^2 + S_j^2} \), where \( S_i \) is the spread of the \( i \)-th MLWF. Then, in Eq. (1) the dipole interaction tensor is

\[
T_{ij}^{ab} = -\frac{3r_{ij}^ar_{ij}^b-r_{ij}^2\delta_{ab}}{r_{ij}^3}\left(\text{erf}\left(\frac{r_{ij}}{\sigma_{ij}}\right) - \frac{2}{\sqrt{\pi} \sigma_{ij}} e^{-\left(\frac{r_{ij}}{\sigma_{ij}}\right)^2} \right) + \frac{4}{\sqrt{\pi} \sigma_{ij}^3} \frac{r_{ij}^a r_{ij}^b}{r_{ij}^3} e^{-\left(\frac{r_{ij}}{\sigma_{ij}}\right)^2}
\]

(4)

where \( a \) and \( b \) specify Cartesian coordinates \((x, y, z)\), \( r_{ij}^a \) and \( r_{ij}^b \) are the respective components of the distance \( r_{ij} \), and \( \delta_{ab} \) is the Kronecker delta function.

Moreover, as in ref. 10, adopting a simple classical theory, the polarizability of an electronic shell of charge \( eZ_i \) and mass \( mZ_i \), tied to a heavy undeformable ion is written as

\[
\alpha_i = \zeta Z_i \frac{e^2}{m\omega_i^2}.
\]

Then, given the direct relation between polarizability and volume,\(^{26}\) we assume that \( \alpha_i \sim \gamma S_i^3 \), where \( \gamma \) is a proportionality constant, so that the orbital volume is expressed in terms of the \( i \)-th MLWF spread, \( S_i \).

Similarly to ref. \(^{24}\), we combine the QHO model, which accurately describes the long-range correlation energy, with a given semilocal, Generalized Gradient Approximation (GGA), functional (PBE\(^{27}\) in our case), which is expected to well reproduce short-range correlation effects, by introducing an empirical parameter \( \beta \) that multiplies the QHO-QHO interaction parameter \( \sigma_{ij} \) in Eq. (3). The three parameters \( \beta \), \( \gamma \), and \( \zeta \) are set up by minimizing the mean absolute relative errors (MARE), measured with respect to high-level, quantum-chemistry reference values relative to the S22 database (see below). By taking PBE\(^{27}\) as the reference DFT functional, we get: \( \beta = 1.39 \), \( \gamma = 0.88 \), and \( \zeta = 1.30 \). In our previous DFT/vdW-WF2\(^{10}\) approach, the constant \( \gamma = 0.87 \) was instead set up by imposing that the exact value for the H atom polarizability \( (\alpha_H = 4.5 \text{ a.u.}) \) is obtained (of course, in the H case, one knows the exact analytical spread, \( S_i = S_H = \sqrt{3} \text{ a.u.} \)). It is clearly reassuring that, in spite of the different adopted recipes, the resulting \( \gamma \) values are very similar.

Note that, differently from ref. \(^{24}\), here the atom-based point of view is replaced by an electron-based point of view, so that the approach is also applicable to systems, such
as metals and semimetals, which cannot be described in terms of assemblies of atoms only weakly perturbed with respect to their isolated configuration. Moreover, differently from the previous DFT/vdW-WF and DFT/vdW-WF2 schemes, in the new DFT/vdW-QHO-WF method it is no longer necessary to subdivide the system into separated fragments, and the certain degree of empiricism associated to the presence of a suitable damping function is now eliminated.

In the specific case of adsorption on metal surfaces, a proper treatment of metal screening effects is mandatory. Although the QHO model intrinsically describes many-body effects in the case of localized fluctuating dipoles, the present approach is not well suited for describing the response of delocalized electrons. In fact, for MLWFs characterized by large spread, the single QHO approximation is less appropriate, as the response of delocalized electrons is expected to be closer to that of a homogeneous electron gas. To this aim, for the H\textsubscript{2}-Cu(111) system, we adopted two different recipes: a “single-layer” approximation, similar to the simplest scheme (DFT/vdW-WF2s3) among those proposed in ref. [11], and a Thomas-Fermi scheme.

In the “single-layer” approach, essentially, vdW effects are only restricted to the interactions of the adparticle with the topmost metal layer; in fact, as a consequence of screening, one expects that the topmost metal atoms give the dominant contribution. We have implemented this by introducing fractional occupation numbers assigned to the MLWFs, as suitable weights to describe screening effects in the metal substrate. In particular, the occupation number assigned to the \(i\)-th WFC is given by:

\[
 f_i = 2 \left(1 - \frac{1}{1 + e^{(z_i - z_r)/\Delta z}}\right),
\]

(6)

where \(z_i\) is the vertical coordinate of the \(i\)-th WFC, the reference level \(z_r\) is taken as the level of the second, topmost surface layer, and we assume that \(\Delta z = \text{(interlayer separation)}/4\); we found that the estimated equilibrium binding energies and adparticle-surface distances exhibit only a mild dependence on the \(\Delta z\) parameter.

Instead in the Thomas-Fermi scheme the potential of Eq. (3) is replaced by

\[
 V_{ij} = \frac{\text{erf}(r_{ij}/\sigma_{ij}) e^{-qr_{ij}}}{r_{ij}},
\]

(7)

where \(q\) is the standard Thomas-Fermi wave vector, \(k_{TF}\), appropriate for the Cu bulk.
metal if both the $i$-th and the $j$-th WFC are inside the metal slab, $q = 0$ if both the WFCs are outside the metal slab, while, in the intermediate cases, $q = k_{TF} r_{in}^{ij} / r_{ij}$, that is $k_{TF}$ is renormalized by considering the portion, $r_{in}^{ij}$, of the $r_{ij}$ segment which is inside the metal slab.

Therefore, the present DFT/vdW-QHO-WF method includes both a short-range damping (to take orbital overlap effects into account) and, where appropriate, a long-range damping (to take metal-screening effects into account).

The calculations have been performed with both the CPMD$^{32}$ and the Quantum-ESPRESSO ab initio package$^{33}$ (in the latter case the MLWFs have been generated as a post-processing calculation using the WanT package$^{34}$). Electron-ion interactions were described using norm-conserving pseudopotentials and the PBE reference DFT functional$^{27}$ which was adopted also in ref. 24 and represents one of the most popular GGA choices.

### III. RESULTS AND DISCUSSION

In order to assess the accuracy of the DFT/vdW-QHO-WF method we have chosen to start by considering the S22 database of intermolecular interactions$^{25}$ a widely used benchmark database, consisting of weakly interacting molecules (a set of 22 weakly interacting dimers mostly of biological importance), with reference binding energies calculated by a number of different groups using high-level quantum chemical methods. In particular, we use the recent basis-set extrapolated CCSD(T) binding energies calculated by Takatani et al.$^{35}$ These binding energies are presumed to have an accuracy of about 0.1 kcal/mol (1% relative error). Table I summarizes the results of our calculations on the S22 database, compared to those obtained by other vdW-corrected DFT schemes, namely our previous DFT/vdW-WF$^{7-9}$ and DFT/vdW-WF$^{10}$ methods, vdW-DF$^{36,37}$, vdW-DF2$^{38}$, VV10$^{39}$ and rVV10$^{40}$ (the revised, computationally much more efficient version of the VV10 method), PBE+TS-vdW$^{41}$ and PBE+MBD$^{21}$. For the sake of completeness we also report data relative to the semiempirical PBE-D3$^{42}$ approach and to the bare, non-vdW-corrected, PBE functional. As can be seen, considering the MARE, the performances of the DFT/vdW-QHO-WF method are good, being only inferior to those of the rVV10, VV10, and PBE+MBD schemes, which nowadays probably represent the most accurate vdW-corrected DFT approaches for noncovalently bound complexes$^{21,48}$. In particular, the mean absolute error (MAE) of DFT/vdW-QHO-WF...
WF (31 meV) is well below the so-called "chemical accuracy" threshold of 1 kcal/mol (about 43 meV), required to attribute a genuine quantitative character to the predictions of an ab initio scheme.

These findings are certainly very promising, however, since the three parameters $\beta$, $\gamma$, and $\zeta$ have been set up by just minimizing the MARE relative to the S22 database (see above), in order to give a stronger assessment of the quality of the method, further tests are required, to check whether good performances are obtained also for other interesting systems, always keeping the same values of the parameters. Therefore we have considered graphite, whose interlayer separation distance and binding energy are notoriously difficult quantities to reproduce by standard DFT approaches. In our calculations graphite was modeled with two graphene layers, with A–B stacking (so, to be precise, the calculations refer to two isolated graphene layers and not to a bulk graphite solid); the periodic cell contained 144 C atoms, and an empty region of about 16 Å width was left among the graphite replicas, in the direction orthogonal to the graphene planes. The in-plane geometry was fixed to the one determined experimentally (C–C distance = 1.421 Å), while the vertical, interlayer distance was optimized. The sampling of the Brillouin Zone was limited to the $\Gamma$ point and, for the DFT/vdW-QHO-WF method, the reference DFT functional was again PBE. Since graphite is a periodically repeated system, each C atom is subject to vdW interactions due not only to the other C atoms contained in the reference supercell, but also to their periodic images. In order to take this effect into account and, at the same time, avoid to have to diagonalize too large QHO matrices, the DFT/vdW-QHO-WF method was applied only to interactions within the reference supercell, while accounting for the interaction with the periodic replicas.

We define the binding energy (per C atom) as $E_b = (E_2 - 2E_1)/N_C$, where $E_2$ and $E_1$ are the total energies relative to the two graphene layers (at the optimized equilibrium distance) and to a single graphene layer, respectively, and $N_C = 144$ is the total number of C atoms contained in the simulation supercell. Note that, in the literature, alternative definitions for the interlayer binding energy of graphite exist,\textsuperscript{43,44} also considering the relationship with the actual experimental measurements: the “exfoliation” energy, $E_e$, is the energy required to remove one graphene plane from the surface of a graphite solid, while the “cleavage” energy, $E_c$, refers to the interaction between two semi-infinite graphite crystals. In any case, the knowledge of $E_b$ at the equilibrium interlayer distance and of the binding energy at a second-layer distance, $E_{bs}$, allows to estimate\textsuperscript{44} $E_e$ and $E_c$: $E_e = E_b + E_{bs}$, $E_c = E_b + 2E_{bs}$.\textsuperscript{7}
No real direct measurement of the interlayer binding energy of graphite has been performed so far and the experimental estimates are quite scattered, ranging from about -60 to -20 meV/atom. At present, probably the most reliable experimental reference value has been obtained from desorption experiments on polyaromatic molecules from a graphite surface, leading to an estimated value of the interlayer binding energy and of the cleavage energy of -52 ±5 and of -61 ±5 meV/atom, respectively.

In Table II the interlayer binding energies and equilibrium distance of graphite, computed by DFT/vdW-QHO-WF, are compared to data obtained by other theoretical schemes, including a Quantum Monte Carlo approach, which is a many-body technique able to account for vdW interactions, and also to some experimental estimates (theoretical data are not corrected by zero-point motion and lattice vibrational contributions). As can be seen, our energetic data are in line with the other theoretical values; moreover, the DFT/vdW-QHO-WF estimate of the interlayer distance turns out to be closer to the experimental reference value (which, differently from the binding energy, is precisely determined) than the distances predicted by the other theoretical schemes.

As our final application test we have considered the interaction of H$_2$ on Cu(111). Adsorption processes on solid surfaces represent a very important topic both from a fundamental point of view and to design and optimize countless material applications. In particular, the adsorption of closed electron-shell particles, such as rare-gas atoms and the H$_2$ molecule on metal surfaces is prototypical for "physisorption" processes, characterized by an equilibrium between attractive, long-range van der Waals (vdW) interactions and short-range Pauli repulsion. For the H$_2$ molecule on low-index Cu surfaces, accurate physisorption data from experiment are available. Actually H$_2$ is the only molecule for which a detailed mapping of the gas-surface interaction potential has been performed with resonance scattering measurements (see ref. 49 and references therein).

For the H$_2$-Cu(111) system we have modeled the metal surface using a periodically-repeated hexagonal supercell, with a ($\sqrt{3} \times \sqrt{3}$)R30° structure and a surface slab made of 15 Cu atoms distributed over 5 layers; moreover, we have adopted the same computational approach of our previous study, but for the replacement of the PW91 functional with the PBE one, for the sake of uniformity with the other calculations performed with DFT/vdW-QHO-WF. Similarly to the graphite case described above and as done in previous applications on adsorption processes, we have also included the vdW interactions of
the MLWFs of the physisorbed H\(_2\) molecule not only with the MLWFs of the underlying surface, within the reference supercell, but also with a sufficient number of periodically-repeated surface MLWFs (in any case, given the \(R^{-6}\) decay of the vdW interactions at large distances, the convergence with the number of repeated images is rapidly achieved). The binding energy has been evaluated for several adsorbate-substrate distances; then the equilibrium distances and the corresponding binding energies have been obtained (as in refs. 11,16) by fitting the calculated points with the function: \(Ae^{-Bz} - C_3/(z - z_0)^3\).

In Table III DFT/vdW-QHO-WF results (DFT/vdW-WF-QHO\(_{SL}\) and DFT/vdW-WF-QHO\(_{TF}\) denote the DFT/vdW-WF-QHO method with metal screening effects included by the single-layer approximation and the Thomas-Fermi scheme described above) are compared to available theoretical and experimental estimates and to corresponding data obtained using our previous DFT/vdW-WF2s schemes\(^{11}\) (in that case using the PW91 reference DFT functional), and other vdW-corrected DFT approaches. As found in the previous studies\(^{11,16}\) the effect of the vdW-corrected schemes is a much stronger bonding than with a pure PBE scheme, with the formation of a clear minimum in the binding energy curve at a shorter equilibrium distance. Moreover, by comparing with unscreened data, obtained by bare DFT/vdW-QHO-WF (we recall that also the other vdW-corrected DFT methods do not take explicitly metallic screening into account), we find that the effect of screening is substantial, leading to reduced binding energies and increased adparticle-substrate equilibrium distances. It is reassuring that the results obtained by using the two different recipes to describe metal screening are very similar.

Both the DFT/vdW-WF-QHO\(_{SL}\) and DFT/vdW-WF-QHO\(_{TF}\) binding energies turn out to slightly underestimate the experimental value, although they are not worse than the predictions of the vdW-DF, vdW-DF2 and rVV10 methods which instead tend to overestimate it. Actually, the discrepancy with respect to the experiment is comparable with the uncertainty associated to the approximate treatment of the metal-screening effect.\(^{11}\)

The DFT/vdW-WF-QHO\(_{SL}\) and DFT/vdW-WF-QHO\(_{TF}\) equilibrium distances of H\(_2\) on Cu(111) are instead much better than with the other methods, with the exception of rVV10. The same is true for the estimated C\(_3\) coefficient if comparison is done with the reference value of Vidali et al.\(^{51}\)
IV. CONCLUSIONS

In summary, we have presented a scheme to include the vdW interactions in DFT by combining the QHO model with the MLWF technique. The method has been applied to the S22 molecular database, and also to extended systems, namely graphite and H$_2$ adsorbed on the Cu(111) metal surface (in this case metal screening effects are taken into account). By comparing the results with those obtained by other vdW-corrected DFT schemes the performances are satisfactory and turn out to be better than those of the previous DFT/vdW-WF and DFT/vdW-WF2 approaches, also based on the use of the MLWFs.

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**TABLE I**: Performance of different schemes on the S22 database of intermolecular interactions.

The errors are measured with respect to basis-set extrapolated CCSD(T) calculations of Takatani et al. \(^\text{35}\) Mean absolute relative errors (MARE in %) and mean absolute errors (MAE in kcal/mol, and, in parenthesis, in meV) are reported.

| method                  | MARE | MAE  |
|-------------------------|------|------|
| DFT/vdW-WF-QHO          | 7.7  | 0.71 [30.9] |
| DFT/vdW-WF              | 9.6  | 0.88 [38.2] |
| DFT/vdW-WF2             | 18.9 | 1.57 [68.1] |
| vDW-DF\(^a\)            | 17.0 | 1.22 [52.9] |
| vDW-DF2\(^b\)           | 14.7 | 0.94 [40.8] |
| VV10\(^b\)              | 4.4  | 0.31 [13.4] |
| rVV10\(^c\)             | 4.3  | 0.30 [13.0] |
| PBE+TS-vdW\(^d,e\)      | 10.3 | 0.32 [13.9] |
| PBE+MBD\(^d\)           | 6.2  | 0.26 [11.3] |
| PBE-D3\(^c,f\)          | 11.4 | 0.50 [21.7] |
| PBE\(^f,g\)             | 55.5 | 2.56 [111.0] |

\(^{a}\text{ref.52}\)
\(^{b}\text{ref.39}\)
\(^{c}\text{ref.40}\)
\(^{d}\text{ref.23}\)
\(^{e}\text{ref.41}\)
\(^{f}\text{ref.42}\)
\(^{g}\text{ref.53}\)
TABLE II: Interlayer binding energy, $E_b$, exfoliation energy, $E_e$, cleavage energy, $E_c$ (see text for the definitions), and interlayer distance, $R$, of graphite.

| method                  | $E_b$ (meV) | $E_e$ (meV) | $E_c$ (meV) | $R$ (Å) |
|------------------------|-------------|-------------|-------------|---------|
| DFT/vdW-WF-QHO         | -37         | -44         | -51         | 3.33    |
| vdW-DF$^a$             | -45         | -48         | -50         | 3.60    |
| “revised DFT”$^b$      | -34         | —           | —           | 3.50    |
| rVV10                  | -38         | -41         | -44         | 3.41    |
| TS-vdW+SCS$^c$         | -55         | —           | —           | 3.37    |
| QMC$^d$                | —           | —           | -60±5       | 3.43±4  |
| expt.$^e$              | —           | -35±10      | —           | 3.34    |
| expt.$^f$              | -52±5       | —           | -61±5       | 3.34    |
| expt.$^g$              | -31±2       | —           | —           | 3.34    |

$^a$ref.43.  $^b$ref.54.  $^c$ref.55.  $^d$ref.44.  $^e$ref.45.  $^f$ref.46.  $^g$ref.47.
TABLE III: Binding energy $E_b$, see text for the definition, equilibrium distance $R$, and estimated $C_3$ coefficient of $H_2$ on Cu(111). DFT/vdW-WF-QHO$_{SL}$ and DFT/vdW-WF-QHO$_{TF}$ denote the DFT/vdW-WF-QHO method with metal screening effects included by the single-layer approximation and the Thomas-Fermi scheme, respectively (see text).

| method               | $E_b$ (meV) | $R$ (Å) | $C_3$ (meVÅ$^3$) |
|----------------------|-------------|---------|------------------|
| DFT/vdW-WF-QHO       | -58         | 3.03    | 1043             |
| DFT/vdW-WF-QHO$_{SL}$| -23         | 3.47    | 647              |
| DFT/vdW-WF-QHO$_{TF}$| -21         | 3.52    | 613              |
| DFT/vdW-WF2s$^a$     | -36↔-26     | 3.40↔3.60 | 984↔1216         |
| vdW-DF$^{a,b}$       | -53         | 3.85    | 2310             |
| vdW-DF2$^{a,b}$      | -39         | 3.64    | 1097             |
| rVV10                | -41         | 3.52    | 1190             |
| DFT-D3$^{b,c}$       | -98         | 2.86    | —                |
| TS-vdW$^{b,d}$       | -66         | 3.20    | —                |
| PBE                  | -6          | 4.10    | —                |
| ref.51               | —           | —       | 673              |
| expt.$^e$            | -29±5       | 3.52    | —                |

$^a$ref.11
$^b$ref.49
$^c$ref.42
$^d$ref.11
$^e$ref.49