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# Assessing the correctness of pressure correction to solvation theories in the study of electron transfer reactions

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Liquid states theories have emerged as a numerically efficient alternative to costly molecular dynamics simulations of electron transfer reactions in solution. In a recent paper [*Chem. Sci.*, 2019, 10, 2130], we introduced the framework to compute energy gap, free energy profile and reorganization free energy using molecular density functional theory. However, this technique, as other molecular liquid state theories, overestimates the bulk pressure of the fluid. Because of the too high pressure, the predicted free energy is dramatically exaggerated. Several attempts were made to fix this issue, either based on simple a posteriori correction or by introducing bridge terms. By studying two model half reactions in water,  $\text{Cl} \rightarrow \text{Cl}^+$  and  $\text{Cl} \rightarrow \text{Cl}^-$ , we assess the correctness of these two types of corrections to study electron transfer reactions. We found that a posteriori correction, because it violates the functional principle, leads to an inconsistency in the definition of the reorganization free energy and should not be used to study electron transfer reactions. The bridge approach, because it is theoretically well grounded, is perfectly suitable for this type of systems.

## I. INTRODUCTION

The widely accepted theory to describe an electron transfer reaction in solution was proposed by Marcus in 1956<sup>1</sup>. Assuming the solvent can be described by a polarization field that responds linearly to the electric field generated by the solute, he derived an expression linking the activation free energy to the reaction free energy. This expression depends on an unique parameter: the reorganization energy. Reorganization energy measures the cost to distort the solvent from the configuration in equilibrium with the reactant to the one in equilibrium with the product, without transferring electron. The polarization varies continuously between the equilibrium values of reactant and product. By computing the free energy of both states for out-of equilibrium polarizations, one can plot the free energies as a function of an appropriate reaction coordinate. This gives rise to the famous Marcus two parabola picture for the free energy profiles.

From a simulation point of view, electron transfer reactions have been mostly investigated using molecular dynamics (MD). Warshel proposed to use the energy gap as the relevant microscopic reaction coordinate<sup>2</sup>. When the probability distribution of the energy gap is Gaussian, the free energy profiles are parabolic with identical curvatures, as predicted by Marcus<sup>3</sup>. The Gaussian behavior has been verified in several studies but some systems deviate from the Marcus picture<sup>4-6</sup>. Resort to numerical simulations of electron transfer reactions is essential to account for such cases, unfortunately computing the free energy profiles with MD remains costly and require the use of biased sampling techniques<sup>7,8</sup>.

We recently proposed an alternative way to compute free energy profiles and reorganization free ener-

gies of electron transfer reactions based on molecular Density Functional Theory (mDFT)<sup>9,10</sup>. Because it allows to compute directly the solvation free energy through functional minimization, it is computationally more efficient than MD. Moreover, mDFT allows a fine description of solvation at the molecular level and a good agreement with MD was found for the  $\text{Cl} \rightarrow \text{Cl}^+$  and the  $\text{Cl} \rightarrow \text{Cl}^-$  electron transfer reactions. The first one is found to follow Marcus theory while the second one is not.

In previous work, the hyper-netted chain (HNC) approximation was used to describe the solute-solvent correlations<sup>11</sup>, neglecting the so-called bridge functional. However, because this functional is a Taylor expansion truncated at second-order, it drastically overestimates the free energy per solvent molecule at gas density<sup>12-14</sup>. This increases considerably the cost to create a solvent cavity and thus the predicted solvation free energy. The reference interaction site model and its 3D variant (3D-RISM), another liquid state theory that have also been extensively used to tackle electron transfer reactions<sup>15-17</sup>, suffer from the same problem<sup>14,18-21</sup>. Because it is a long-standing problem, several attempts were made to fix it. By noticing that the gas phase free energy is directly linked to the pressure, simple a-posteriori corrections were proposed<sup>14,22,23,19,24-26</sup>. Essentially, they consist in evaluating the partial molar volume (PMV) created by the solute and applying a free energy correction proportional to it.

A more rigorous approach is to fix the defect of the functional by introducing an approximate bridge term, to go beyond second order. Several models of bridge functional have been proposed, either based on hard sphere theory<sup>27-29</sup> or weighted density approximation (WDA)<sup>13,30,31</sup>.

In this paper, we evaluate the impact of those two types of correction on the free energy profiles and reorganization free energies predicted for two model elec-

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tron transfer reactions:  $\text{Cl} \rightarrow \text{Cl}^+$  and  $\text{Cl}^- \rightarrow \text{Cl}$ . For a posteriori correction we selected the widely used pressure correction (PC)<sup>14,19</sup> while the bridge functional is the recently proposed angular independent WDA functional<sup>13</sup>.

## II. THEORY

We remind here some basics of mDFT which are essential for the comprehension of this paper. Thorough descriptions can be found in previous reports<sup>9,10,22</sup>.

In mDFT, solvent and solute molecules are described by rigid models interacting through classical forcefield. The solvation free energy of the solute can be computed by minimizing the solvent functional with respect to the spatially and orientationally dependent solvent density  $\rho(\mathbf{r}, \mathbf{\Omega})$ . We introduce the following notation  $\mathbf{x} \equiv (\mathbf{r}, \mathbf{\Omega})$  for concision. The functional to be minimized is

$$F[\rho(\mathbf{x})] = F_{\text{id}}[\rho(\mathbf{x})] + F_{\text{ext}}[\rho(\mathbf{x})] + F_{\text{exc}}[\rho(\mathbf{x})]. \quad (1)$$

Its minimum is reached for the equilibrium solvent density,  $\rho_{\text{eq}}$ . In equation 1,  $F_{\text{id}}$  corresponds to the entropy of the non-interacting liquid

$$F_{\text{id}}[\rho] = k_B T \int \left[ \rho(\mathbf{x}) \ln \left( \frac{\rho(\mathbf{x})}{\rho_b} \right) - \rho(\mathbf{x}) + \rho_b \right] d\mathbf{x} \quad (2)$$

where  $k_B$  is the Boltzmann constant,  $\rho_b$  is the homogeneous bulk solvent density and  $T$  is the temperature.

The second term of equation 1 is due to solute-solvent interaction and can be expressed as

$$F_{\text{ext}}[\rho] = \int \rho(\mathbf{x}) V(\mathbf{x}) d\mathbf{x} \quad (3)$$

where  $V$  is the the external potential energy exerted by the solute.

Solvent-solvent interactions are collected in the last term of equation 1, that is the excess functional  $F_{\text{exc}}$ . Expanding it around the density  $\rho_b$  of the homogeneous fluid taken as a reference, and truncating the expansion at second order gives rise to the HNC functional. All the higher order correlations are then swept into the unknown bridge functional  $F_B$ ,

$$\begin{aligned} F_{\text{exc}}[\rho] &= F_{\text{HNC}}[\rho] + F_B[\rho] \\ &= -\frac{1}{2} k_B T \iiint [\Delta\rho(\mathbf{r}_1, \mathbf{\Omega}_1) c(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{\Omega}_1, \mathbf{\Omega}_2) \\ &\quad \times \Delta\rho(\mathbf{r}_2, \mathbf{\Omega}_2)] d\mathbf{r}_1 d\mathbf{\Omega}_1 d\mathbf{r}_2 d\mathbf{\Omega}_2 + F_B[\rho] \end{aligned} \quad (4)$$

where  $c$  is the direct correlation function of homogeneous fluid at density  $\rho_b$  and  $\Delta\rho = \rho - \rho_b$ <sup>11</sup>.

We evaluate two types of pressure correction in this paper. The PMV correction takes the following expression<sup>14,19</sup>

$$F_B^{\text{PMV}} = \rho_b k_B T \left( 1 - \frac{\rho_b}{2} \hat{c}(k=0) \right) \int \frac{\rho_{\text{eq}}(\mathbf{x}) - \rho_b}{\rho_b} d\mathbf{x} \quad (5)$$

where  $\hat{c}$  denotes the Fourier transform of the direct correlation function. Since equation 5 does not depend on the density  $\rho$ , such a correction does not modify the optimization process. The equilibrium density remains the same as the one obtained using the HNC functional.

For the bridge correction, we take the recently proposed spherical WDA functional<sup>13</sup>

$$F_B^{\text{WDA}}[\rho] = \frac{k_B T}{n_b^3} \iint a \left[ \int \Delta\rho(\mathbf{r}', \mathbf{\Omega}) \times w(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \right]^3 d\mathbf{\Omega} d\mathbf{r} \quad (6)$$

the value of  $a$  is uniquely defined by imposing the correct pressure<sup>13</sup> and  $w$  is a Gaussian weighting function

$$w(r) = (2\pi\sigma_w^2)^{-3/2} \exp(-r^2/2\sigma_w^2) \quad (7)$$

with  $\sigma_w = 1 \text{ \AA}$ .

We now turn our attention to the study of electron transfer half-reaction of the type  $\text{Red} \rightarrow \text{Ox} + e^-$ , and remind how it is possible to compute free energy profiles and reorganization free energies using mDFT.

We start by introducing a set of external potentials defined as a linear combination between the external potential of the Ox (denoted by 0) and Red (denoted by 1) states

$$V_\eta = V_0 + \eta(V_1 - V_0). \quad (8)$$

where  $\eta$  is a real number.

Minimizing the functional in equation 1 using the external potentials in equation 8 generate a set of solvent densities  $\rho_\eta$ . While  $\rho_0$  and  $\rho_1$  correspond to the equilibrium solvent densities for the Ox and the Red states respectively, any other value of  $\eta$  defines a solvent density  $\rho_\eta$  that is out of equilibrium for both states. It becomes possible to compute the free energy of an electronic state  $\alpha = 0$  or 1, solvated in a solvent density  $\rho_\eta$ , by evaluating the associated functional:  $F_\alpha[\rho_\eta]$ . The definition of the two solvent reorganization free energies comes out naturally

$$\lambda_0 = F_0[\rho_1] - F_0[\rho_0] \text{ and } \lambda_1 = F_1[\rho_0] - F_1[\rho_1]. \quad (9)$$

We then defined the energy gap as

$$\langle \Delta E \rangle_\eta = \int \rho_\eta(\mathbf{x}) [V_1(\mathbf{x}) - V_0(\mathbf{x})] d\mathbf{x} \quad (10)$$

and showed that it is an appropriate reaction coordinate since there is a one to one mapping between the energy gap and the solvent density<sup>10</sup>

$$\eta \leftrightarrow V_\eta \leftrightarrow \rho_\eta \leftrightarrow \langle \Delta E \rangle_\eta. \quad (11)$$

The free energy of any state is therefore a function of  $\langle \Delta E \rangle_\eta$  and it is possible to compute the free energy profile associated to state  $\alpha$  as a function of this reaction coordinate

$$F_\alpha(\langle \Delta E \rangle_\eta) \equiv F_\alpha[\rho_\eta]. \quad (12)$$

### III. COMPUTATIONAL DETAILS

We study two model electron transfer reactions:  $\text{Cl} \rightarrow \text{Cl}^+$  and  $\text{Cl}^- \rightarrow \text{Cl}$  in water. The solute is modeled by one Lennard-Jones site, with  $\sigma=4.404 \text{ \AA}$ , and  $\epsilon=0.4190 \text{ kJ/mol}$ . We consider 3 oxidation states corresponding to  $\text{Cl}^-$ ,  $\text{Cl}^{(0)}$  and  $\text{Cl}^+$ . We use a Lennard-Jones cut-off of  $10 \text{ \AA}$  with long range corrections<sup>32</sup>. Water is described using the SPC/E model. We generate a series of biased external potential by varying the atomic charge of the solute between  $-1.2 \leq q \leq 2$  with a step of  $1/30$  elementary charge. We use a  $40 \times 40 \times 40 \text{ \AA}^3$  box with  $120^3$  spatial grid points and 196 possible orientations per spatial point with periodic boundary condition. We use the type C correction of Hünenberger<sup>33,34</sup> due to interaction between the solute and its periodic replica. The temperature is fixed at  $298.15 \text{ K}$ .

### IV. RESULTS AND DISCUSSIONS

#### A. partial molar volume correction

The free energy profiles of the two half-reactions calculated using the HNC functional with and without the PMV correction are displayed in figure 1. All minima are shifted to zero to ease the comparison with the curves computed by Hartnig et al. using MD<sup>4</sup>. The agreement between the free energy profiles obtained using MD and MDFT is satisfactory for the neutral solute. However, important deviations are observed in the case of the cation and the anion. This is a known defect of the HNC functional which is not able to properly render the hydrogen bond network of water that is essential for the solvation of ions. This is due to the truncation of the functional expansion at second order. The two types of corrections studied in this paper cannot resolve this issue because of their lack of angular dependency.

At first glance, including the PMV correction do not seem to deeply modify the shape of the curve. However, a closer look reveals that the positions of the minima are shifted. This is especially true for the ions where the minima are shifted toward zero. This might appear surprising since the energy gap defined in equation 10 solely depends on the density  $\rho_\eta$  which is not modified by the PMV correction.

In fact, the shift of the minima is a consequence of a pathological defect of this correction. This is visible in figure 2 where the free energy profiles of the ions are depicted as a function of the charge  $q$  of the fictitious solute:  $q = \eta$  for the  $\text{Cl} \rightarrow \text{Cl}^+$  reaction and  $q = -\eta$  for the  $\text{Cl}^- \rightarrow \text{Cl}$  reaction. The minima of the PMV corrected free energy profiles no longer correspond to  $q = 1$  and  $q = -1$ . Equivalently, this means that the minimum of the free energy curve is not reached for the equilibrium solvent density of the solute. This is a violation of the DFT variational principle which is not surprising since the PMV correction is not properly

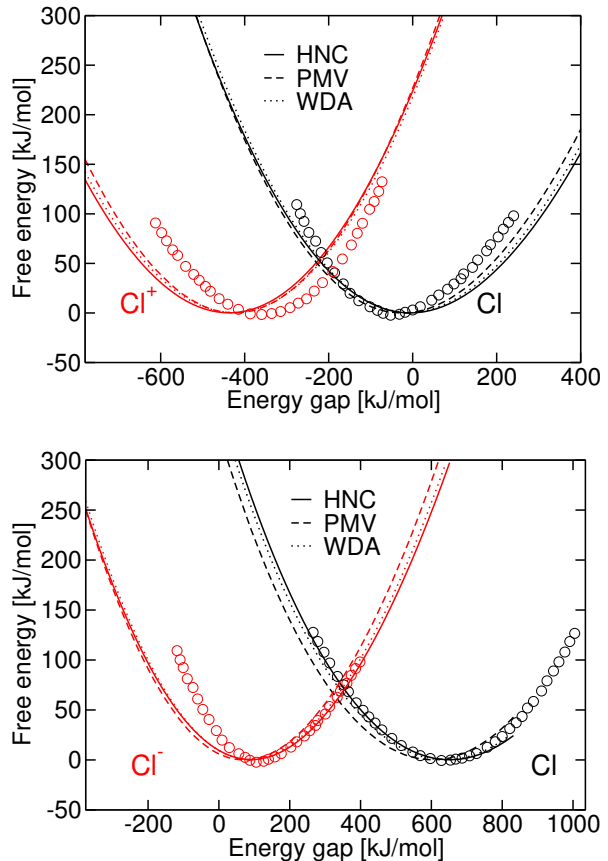


FIG. 1. Free energy profiles of  $\text{Cl} \rightarrow \text{Cl}^+$  and the  $\text{Cl}^- \rightarrow \text{Cl}$  electron transfer reactions computed using the HNC functional with and without (dashed) the PMV correction and using the WDA (dotted) bridge functional. The MD data obtained by Hartnig et al<sup>4</sup> are the circles.

integrated in the classical DFT formalism. It is simply an a posteriori correction that does not influence the optimization. This might be acceptable when the objective is to reproduce some reference solvation free energies<sup>14,19,20,22,23,26</sup> but it is problematic to study electron transfer reactions. Indeed, the two ways to compute the reorganization free energies, either from equation 9 or from the graphical definition, i.e. as the difference between the value of the free energy of one state at the abscissa corresponding to the minimum of the second state and the value at its minimum do not coincide anymore.

Reorganization free energies are given in table I. Note that there are two sets of values for the neutral chlorine since the value of  $\lambda$  depends on the choice of the second oxidation state. Solvent reorganization free energies of  $\text{Cl}$  and  $\text{Cl}^+$  computed with the HNC functional are similar indicating that this electron transfer reaction is well described using Marcus Theory while the  $\text{Cl}^- \rightarrow \text{Cl}$  reaction deviates from Marcus theory. These results are consistent with MD simulations<sup>4</sup>. When the PMV correction is added, both electron transfer reactions seem to deviate from Marcus theory since the reorganization free energies of ions differ from the one of the associated neutral state. More-

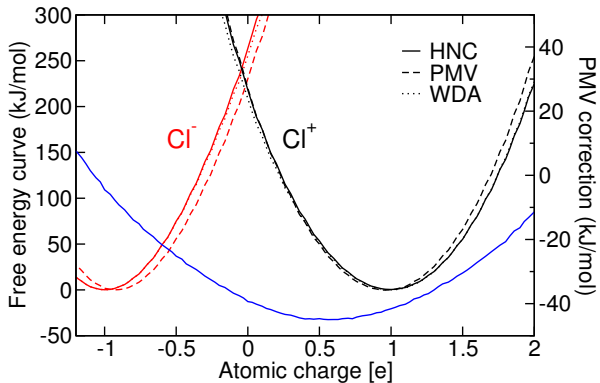


FIG. 2. Free energy of  $\text{Cl}^+$  and  $\text{Cl}^-$  computed using the HNC functional without (full) and with (dashed) the PMV correction and using the WDA (dotted) bridge functional as a function of the charge of the fictitious solute. The value of the PMV correction is also displayed as a function of the charge of the fictitious solute.

$\lambda$	HNC	PMV (eq 9)	PMV graphical	WDA
Cl	297	332	287	295
$\text{Cl}^-$	264	229	230	255
Cl	218	220	220	209
$\text{Cl}^+$	214	212	197	209

TABLE I. Solvent reorganization free energies (in kJ/mol) calculated with the HNC functional, with the PMV correction using equation 9, with the PMV correction using the graphical definition and with the WDA functional.

over, the reorganization free energies computed using equation 9 differ by up to 25 kJ/mol from the one computed with the graphical definition.

The evolution of the energy gap as a function of  $q$  is displayed in figure 3. We recall that values of  $q$  between 0 and 1 correspond to the  $\text{Cl} \rightarrow \text{Cl}^+$  while the value between 0 and -1 corresponds to  $\text{Cl}^- \rightarrow \text{Cl}$ . When an electron transfer reaction is following Marcus theory, the energy gap should vary linearly. This is the case between  $q = 0$  and  $q = 1$ , while the linearity is not respected between  $q = 0$  and  $q = -1$ . This is consistent with the conclusions drawn examining the reorganization free energies computing using the HNC functional and with the MD results: the  $\text{Cl} \rightarrow \text{Cl}^+$  reaction follows Marcus theory while the  $\text{Cl}^- \rightarrow \text{Cl}$  reaction does not. Since the energy gap is not modified by the PMV correction, the linear behavior observed for the  $\text{Cl} \rightarrow \text{Cl}^+$  is in contradiction with the different values of  $\lambda$  of table I. This is another proof of the inappropriateness of the PMV correction to study electron transfer reactions.

## B. Weighted density bridge functional

The same electron transfer reactions were studied using the WDA functional of equation 6 and the prediction for the free energy profiles as a function of the

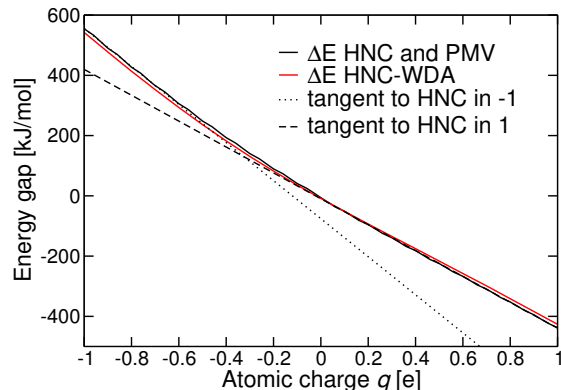


FIG. 3. Vertical energy gap computed using the HNC (solid black) and WDA functional (solid red) as a function of the atomic charge. The dotted and dashed lines are the tangent to the HNC curve in  $q = -1$  and  $q = 1$  respectively.

energy gap or of the solute charge are given in figures 1 and 2 respectively. Adding WDA bridge has a limited impact on the free energy profile as compared to the HNC predictions. More importantly, the minimum of the free energy curve of the cation (resp. anion) is correctly reached for the solute with charge  $q = 1$  (resp.  $q = -1$ ). This is because the WDA correction has a functional form and the variational principle is respected. The reorganization free energies predicted with the WDA functional are slightly reduced with respect to the one predicted using HNC but the overall conclusion is recovered:  $\text{Cl} \rightarrow \text{Cl}^+$  follows Marcus picture while  $\text{Cl} \rightarrow \text{Cl}^-$  does not. This is also supported by the evolution of the energy gap as a function of the atomic charge in figure 3.

We now attempt to understand why the reorganization free energy of the ions are reduced when the WDA bridge is used. We introduce the free energy difference for a state  $\alpha$  as

$$\Delta F_\alpha(\eta) = F_\alpha^{\text{WDA}}(\eta) - F_\alpha^{\text{HNC}}(\eta) \quad (13)$$

$$= \Delta F_\alpha^{\text{ext}}(\eta) + \Delta F_\alpha^{\text{int}}(\eta) \quad (14)$$

where  $\Delta F_\alpha^{\text{ext}}$  is the difference of the external functionals defined by equation 3 and  $\Delta F_\alpha^{\text{int}}$  is the contribution of the ideal and excess term in equation 1. Since the WDA functional modifies the minimization process, the equilibrium solvent densities associated to the same  $\eta$  differ for both corrections in equation 13.

Using equation 9, the difference of the reorganization free energies obtained with and without the WDA functional can be expressed as

$$\Delta \lambda_\alpha = \lambda_\alpha^{\text{WDA}} - \lambda_\alpha^{\text{HNC}} = \Delta F_\alpha(0) - \Delta F_\alpha(\alpha) \quad (15)$$

$$\approx \Delta F_\alpha^{\text{elec}}(0) - \Delta F_\alpha^{\text{elec}}(\alpha) \quad (16)$$

where  $\Delta F_\alpha^{\text{elec}}$  is the electrostatic part of external functional difference. In equation 16, we assume that since the considered species are ions, the main contribution

is due to the electrostatic, i.e  $\Delta F^{\text{int}}$  and the Lennard-Jones contributions can be neglected. As long as we are considering spherical ions, the electrostatic potential is spherically symmetric, so is the polarization of the solvent. The equilibrium dipolar polarization density of the fluid can be computed from the equilibrium solvent density as

$$\frac{P(r, \Omega)}{\mu_0} = \int \rho_{\text{eq}}(r, \Omega) \Omega d\Omega \quad (17)$$

where  $\mu_0$  is the molecular dipole of the solvent molecule. The spherically averaged radial component of the solvent equilibrium polarization around each ion are displayed in figure 4.

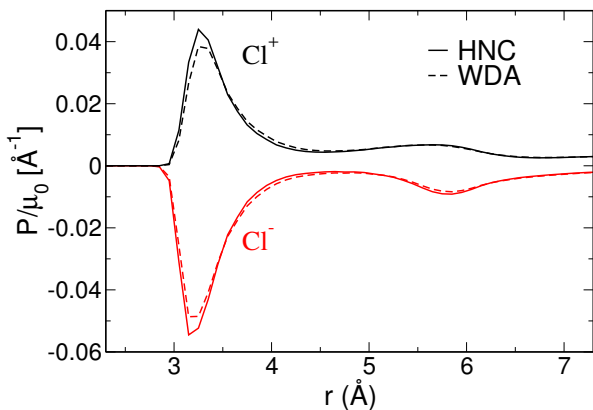


FIG. 4. Equilibrium radial polarization density around  $\text{Cl}^-$  and  $\text{Cl}^+$  computed by HNC and WDA

The WDA functional reduces the polarization of the solvent in the vicinity of the charged solutes, as evidenced by the decrease of the first peaks in figure 4. Since the polarization is reduced, the ion is destabilized by the WDA functional when immersed in its equilibrium density,  $\Delta F_{\alpha}^{\text{elec}}(\alpha) > 0$ . On the contrary, the equilibrium density of the oppositely charged ion is less destabilizing  $\Delta F_{\alpha}^{\text{elec}}(-\alpha) < 0$ . Finally, the WDA correction being angular independent we can expect the polarization around the neutral solute to be almost unchanged  $\Delta F_{\alpha}^{\text{elec}}(0) \approx 0$ . With this simple analysis and using equation 16 we recover the decrease of the reorganization free energy observed in table I. A verification of the hypothesis made here and a more detailed examination of the evolution of the different quantities entering equations 14-15 is available in SI.

## V. CONCLUSIONS

In this paper we studied the appropriateness of two corrections to the HNC functional to study aqueous electron transfer reactions with molecular density functional theory. First, we examine a simple a posteriori correction of the pressure which has been widely used with different expression in mDFT and 3D-RISM<sup>14,18,19,21-23,26</sup>. Despite its success to predict solvation free energy in good agreement with reference simulations and experiments, this correction

should not be used to study electron transfer reactions. The minima of the free energy profile does not correspond to the equilibrium solvent configuration when this correction is used because it modifies the free energy without affecting the functional optimization. The reorganization free energies becomes ill-defined: the graphical definition do not coincide with the mathematical expression. Moreover, we have shown that using any of the two definitions of the reorganization free energy lead to a behavior deviating from the Marcus picture for  $\text{Cl} \rightarrow \text{Cl}^+$  reaction in disagreement with MD simulations and HNC mDFT calculations. This deviation from Marcus theory is not recovered when examining the evolution of the energy gap, which is a final evidence for the inconsistency of the pressure correction.

We then turned to another type of correction, a so-called bridge functional which is trying to recover some of the contribution due to the terms beyond the quadratic approximation of the HNC functional. We have chosen to use the recent and simple angular independent weighted density functional<sup>13</sup> that was shown to properly reproduce the solvation free energies of hydrophobic solutes. Since this bridge has a functional form, the equilibrium density is modified and this approach does not suffer from the flaws of the PMV correction. There are no ambiguities in the definitions of the reorganization free energies, and we recover results consistent with MD simulations and HNC mDFT calculations:  $\text{Cl} \rightarrow \text{Cl}^+$  follows Marcus picture while  $\text{Cl}^- \rightarrow \text{Cl}$  deviates from it. Overall, the WDA functional does not modify significantly the results obtained without correction<sup>10</sup>. This might be because it is an angular independent correction, having a low impact on the polarization of the solvent which is the dominant effect for ions.

## VI. ACKNOWLEDGEMENT

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## VII. DATA AVAILABILITY STATEMENT

Data available on request from the authors

<sup>1</sup>R. A. Marcus. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. *J. Chem. Phys.*, 24:966-978, 1956.

<sup>2</sup>Arieh Warshel. Dynamics of reactions in polar solvents. Semi-classical trajectory studies of electron-transfer and proton-transfer reactions. *J. Phys. Chem.*, 86:2218-2224, 1982.

<sup>3</sup>J. Blumberger and M. Sprik. Redox Free Energies from Vertical Energy Gaps: Ab Initio Molecular Dynamics Implementation. In Mauro Ferrario, Giovanni Ciccotti, and Kurt Binder, editors, *Computer Simulations in Condensed Matter Systems: From Materials to Chemical Biology Volume 2*, volume 704, pages 481-506. Springer Berlin Heidelberg, Berlin, Heidelberg, 2006.

- <sup>4</sup>Christoph Hartnig and Marc T. M. Koper. Molecular dynamics simulations of solvent reorganization in electron-transfer reactions. *J. Chem. Phys.*, 115:8540–8546, 2001.
- <sup>5</sup>Jochen Blumberger. Cuaq+/Cuaq2+ Redox Reaction Exhibits Strong Nonlinear Solvent Response Due to Change in Coordination Number. *Journal of the American Chemical Society*, 130:16065–16068, 2008.
- <sup>6</sup>Rodolphe Vuilleumier, Kafui A. Tay, Guillaume Jeanmairet, Daniel Borgis, and Anne Boutin. Extension of Marcus Picture for Electron Transfer Reactions with Large Solvation Changes. *J. Am. Chem. Soc.*, 134:2067–2074, 2012.
- <sup>7</sup>Gregory King and Arieh Warshel. Investigation of the free energy functions for electron transfer reactions. *J. Chem. Phys.*, 93:8682–8692, 1990.
- <sup>8</sup>Joost VandeVondele, Ruth Lynden-Bell, Evert Jan Meijer, and Michiel Sprik. Density Functional Theory Study of Tetrathiafulvalene and Thianthrene in Acetonitrile: Structure, Dynamics, and Redox Properties. *J. Phys. Chem. B*, 110:3614–3623, 2006.
- <sup>9</sup>Daniel Borgis, Lionel Gendre, and Rosa Ramirez. Molecular Density Functional Theory: Application to Solvation and Electron-Transfer Thermodynamics in Polar Solvents. *J. Phys. Chem. B*, 116:2504–2512, 2012.
- <sup>10</sup>Guillaume Jeanmairet, Benjamin Rotenberg, Maximilien Levesque, Daniel Borgis, and Mathieu Salanne. A molecular density functional theory approach to electron transfer reactions. *Chem. Sci.*, 10:2130–2143, 2019.
- <sup>11</sup>Lu Ding, Maximilien Levesque, Daniel Borgis, and Luc Belloni. Efficient molecular density functional theory using generalized spherical harmonics expansions. *J. Chem. Phys.*, 147:094107, 2017.
- <sup>12</sup>Gerald Rickayzen and Andreas Augousti. Integral equations and the pressure at the liquid-solid interface. *Molecular Physics*, 52:1355–1366, 1984.
- <sup>13</sup>Daniel Borgis, Sohvi Luukkonen, Luc Belloni, and Guillaume Jeanmairet. Simple Parameter-Free Bridge Functionals for Molecular Density Functional Theory. Application to Hydrophobic Solvation. *J. Phys. Chem. B*, 124:6885–6893, 2020.
- <sup>14</sup>Volodymyr P. Sergiievskiy, Guillaume Jeanmairet, Maximilien Levesque, and Daniel Borgis. Fast Computation of Solvation Free Energies with Molecular Density Functional Theory: Thermodynamic-Ensemble Partial Molar Volume Corrections. *J. Phys. Chem. Lett.*, 5:1935–1942, 2014.
- <sup>15</sup>Tsuyoshi Yamaguchi and Norio Yoshida. Nonequilibrium free-energy profile of charge-transfer reaction in polarizable solvent studied using solvent-polarizable three-dimensional reference interaction-site model theory. *The Journal of Chemical Physics*, 153:034502, 2020.
- <sup>16</sup>Song-Ho Chong and Fumio Hirata. The Free Energy Profiles for the Electron Transfer Reactions Calculated from the Integral Equation Method of Liquids. *Molecular Simulation*, 16:3–17, 1996.
- <sup>17</sup>Song-Ho Chong, Shin-ichi Miura, Gautam Basu, and Fumio Hirata. Molecular Theory for the Nonequilibrium Free Energy Profile in Electron Transfer Reaction. *The Journal of Physical Chemistry*, 99:10526–10529, 1995.
- <sup>18</sup>Dirk Gillespie. Restoring the consistency with the contact density theorem of a classical density functional theory of ions at a planar electrical double layer. *Physical Review E*, 90:052134, 2014.
- <sup>19</sup>Volodymyr Sergiievskiy, Guillaume Jeanmairet, Maximilien Levesque, and Daniel Borgis. Solvation free-energy pressure corrections in the three dimensional reference interaction site model. *J. Chem. Phys.*, 143:184116, 2015.
- <sup>20</sup>Maksim Misin, David S. Palmer, and Maxim V. Fedorov. Predicting Solvation Free Energies Using Parameter-Free Solvent Models. *The Journal of Physical Chemistry B*, 120:5724–5731, 2016.
- <sup>21</sup>Maksim Misin, Petteri A. Vainikka, Maxim V. Fedorov, and David S. Palmer. Salting-out effects by pressure-corrected 3D-RISM. *The Journal of Chemical Physics*, 145:194501, 2016.
- <sup>22</sup>Sohvi Luukkonen, Maximilien Levesque, Luc Belloni, and Daniel Borgis. Hydration free energies and solvation structures with molecular density functional theory in the hypernetted chain approximation. *J. Chem. Phys.*, 152:064110, 2020.
- <sup>23</sup>Anton Robert, Sohvi Luukkonen, and Maximilien Levesque. Pressure correction for solvation theories. *J. Chem. Phys.*, 152:191103, 2020.
- <sup>24</sup>David S. Palmer, Andrey I. Frolov, Ekaterina L. Ratkova, and Maxim V. Fedorov. Towards a universal method for calculating hydration free energies: a 3D reference interaction site model with partial molar volume correction. *J. Phys.: Condens. Matter*, 22:492101, 2010.
- <sup>25</sup>Ekaterina L. Ratkova, Gennady N. Chuev, Volodymyr P. Sergiievskiy, and Maxim V. Fedorov. An Accurate Prediction of Hydration Free Energies by Combination of Molecular Integral Equations Theory with Structural Descriptors. *J. Phys. Chem. B*, 114:12068–12079, 2010.
- <sup>26</sup>Maksim Misin, Maxim V. Fedorov, and David S. Palmer. Communication: Accurate hydration free energies at a wide range of temperatures from 3D-RISM. *J. Chem. Phys.*, 142:091105, 2015.
- <sup>27</sup>M. Oettel. Integral equations for simple fluids in a general reference functional approach. *J. Phys.: Condens. Matter*, 17:429–452, 2005.
- <sup>28</sup>Maximilien Levesque, Rodolphe Vuilleumier, and Daniel Borgis. Scalar fundamental measure theory for hard spheres in three dimensions: Application to hydrophobic solvation. *J. Chem. Phys.*, 137:034115, 2012.
- <sup>29</sup>Jia Fu, Yu Liu, and Jianzhong Wu. Fast prediction of hydration free energies for SAMPL4 blind test from a classical density functional theory. *J Comput Aided Mol Des*, 28:299–304, 2014.
- <sup>30</sup>Guillaume Jeanmairet, Maximilien Levesque, and Daniel Borgis. Molecular density functional theory of water describing hydrophobicity at short and long length scales. *J. Chem. Phys.*, 139:154101, 2013.
- <sup>31</sup>Guillaume Jeanmairet, Maximilien Levesque, Volodymyr Sergiievskiy, and Daniel Borgis. Molecular density functional theory for water with liquid-gas coexistence and correct pressure. *J. Chem. Phys.*, 142:154112, 2015.
- <sup>32</sup>Daan Frenkel and Berend Smit. *Understanding molecular simulation: from algorithms to applications*. Academic Press, second edition edition, 2002.
- <sup>33</sup>Mika A. Kastholz and Philippe H. Hünenberger. Computation of methodology-independent ionic solvation free energies from molecular simulations. II. The hydration free energy of the sodium cation. *J. Chem. Phys.*, 124:224501, 2006.
- <sup>34</sup>M. A. Kastholz and Philippe H. Hünenberger. Computation of methodology-independent ionic solvation free energies from molecular simulations. I. The electrostatic potential in molecular liquids. *J. Chem. Phys.*, 124:124106, 2006.