

3D wavelet treatment of solvated bipolaron and polaron.

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Abstract

Three-dimensional discrete tensor wavelets are applied to calculate wave functions of excess electrons solvated in polar liquids. The orthogonal Coifman basis set is used to approximate the wave functions and to minimize the free energy of the system. The scheme is applied to calculate properties of solvated electrons forming a bipolaron. The quality of approximation is verified by calculations of the free energy of a solvated electron and the bipolaron formation. The obtained results indicate that the proposed algorithm is fast and may be very efficient for calculating the electronic structure of solvated molecular solutes.

keywords: tensor wavelets, solvated bipolaron, hydration

I. INTRODUCTION

The wavelet technique [1]-[8] is one of the most important recent developments which allows one to apply a multiscale analysis to the problems exhibiting widely varying length scales [1]. Such problems abound in various fields of computational chemistry [9]-[19]. The special features of wavelets such as (bi)orthogonality and vanishing moments result in the fact that the wavelets are actively used in calculations of electronic structure [15] - [19]. In general, wavelets are to be a universal basis for the study of multiscale processes and can be applied not only to the quantum but also to the mixed quantum-classical systems, and even to classical liquids. Our preliminary study [20] has indicated that wavelets are a suitable and powerful instrument for accurate approximation of radial distribution functions of hydrated ions and hydrophobic solutes with a small number of approximating coefficients. Using the discrete wavelet transform, we have developed a new algorithm to solve integral equations for simple and molecular liquids [21], [22].

The question we want to address here is the extension of the wavelet technique to the mixed quantum-classical systems. We will apply the wavelets to the problem of excess electrons forming the polaron and bipolaron states in polar liquids, which are an object of the intensive theoretical investigation and computer simulations [23]-[30]. Numerous experimental techniques have been developed and some extensive experimental evidence on the behavior of solvated electrons in various media has been accumulated [31]-[32]. Excess electrons solvated in polar liquids provide a simple example of the mixed quantum-classical systems, which exhibit a large number of various effects. Solvated electrons may serve as an excellent test for verification of various theoretical approaches [33]- [39]. These studies have shown that excess electrons in polar liquids can reveal quite intriguing properties such as polaron and bipolaron formations, as well as multielectronic clustering.

Regarding the bipolaron problem we have recently developed an extended DFT method based on wavelets [40] that allows us to calculate the properties of solvated electrons and the local solvent structure around such complexes. We have developed a microscopic model in which the electrons are treated within the Kohn–Sham formalism, while the solvent via the integral equations (IE) theory. We applied the wavelets in both the quantum and the classical domains and, as a result, reduced the problem to the direct minimization of the free energy functional depending on the electron and solvents densities. For solving the obtained

integral equations we used the wavelet scheme [22], [41] but assumed the spherical symmetry of the density functions. In this case we used the one-dimensional Fast Wavelet Transform (FWT) that strongly reduced the computational cost. Despite the obtained results the model proposed in [40] has obvious constraints due to the radial dependent distribution functions of electrons and solvent. Till now there is no reliable wavelet scheme for solving the three-dimensional IE.

The goal of this work is to extend the proposed method to the true three-dimensional (3D) structure of the wave functions of excess electrons in polar liquids. For this purpose we use the three dimensional Fast Wavelet Transform (3DFWT) based on the tensor product of one-dimensional (1D) wavelet functions [1], [18]. As there is a number of brilliant reviews devoted to the wavelets in general and to the concrete problem of the multidimensional wavelet transform we have restricted ourselves only to brief discussion of the tensor-product multidimensional wavelet transform. To make the presentation of our formulas more simple we use the atomic system of units.

II. THE FREE ENERGY FUNCTIONAL

In general, a reliable model of solvated electrons should take into account the microscopic nature of electron-solvent interactions and use the input data on the molecular structure of liquid and solute. Examples of such treatment are described in [40] and [41]. However, we concentrate here on the application of 3D wavelet scheme and use for simplicity the semicontinual parametrization of electron-solvent and electron-exchange interactions [28], [30]. In this case the free energy of an excess electron (polaron) solvated in a polar liquid can be written as [30]:

$$F_p[\Psi] = T + V_{ex} = T - \frac{1}{2} \left(1 - \frac{1}{\varepsilon}\right) \int \int d\mathbf{r} d\mathbf{r}' \frac{\Psi^2(\mathbf{r})\Psi^2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_p^{cav}, \quad (1)$$

where Ψ is the electron wave function, T is the electron kinetic energy, V_p^{cav} is the so-called energy of the cavity formation which can be approximated as:

$$V_p^{cav} \approx \frac{4\pi}{3} \rho k_B T r_p^3, \quad (2)$$

where r_b is the mean polaron radius:

$$r_p = \left[\int \Psi^*(\mathbf{r}) \mathbf{r}^2 \Psi(\mathbf{r}) d\mathbf{r} \right]^{1/2}. \quad (3)$$

For the solvated bipolaron the total free energy can be written as [30]:

$$F_b[\Psi, \Psi_2] = T_1 + T_2 + \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\Psi_2^2(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + V_{ex}[\Psi(\mathbf{r}_1), \Psi(\mathbf{r}_2)], \quad (4)$$

where Ψ, Ψ_2 are the one- and two- electron wave functions, and T_i are kinetic terms

$$T_i = -0.5 \int \int dr_1 dr_2 \Psi_2(r_1, r_2) \nabla_i^2 \Psi_2(r_1, r_2), \quad (5)$$

while the lower subscript denotes the coordinate of the corresponding electron, and V_{ex} is the part of energy due to the external potential. For strongly polar liquids this potential can be approximated as [30]:

$$V_{ex} = -\frac{4}{2} \left(1 - \frac{1}{\varepsilon}\right) \int \int dr_1 dr_2 \frac{\Psi^2(\mathbf{r}_1) \Psi^2(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} + V_b^{cav}, \quad (6)$$

where ε is the permittivity of the liquids and V_b^{cav} is the energy of the cavity formation which can be also approximated:

$$V_b^{cav} \approx \frac{4\pi}{3} \rho k_B T r_b^3, \quad (7)$$

where r_b is the mean bipolaron radius:

$$r_b = 0.5 \left[\left(\int \Psi^*(\mathbf{r}_1) \mathbf{r}_1^2 \Psi(\mathbf{r}_1) d\mathbf{r}_1 \right)^{1/2} + \left(\int \Psi^*(\mathbf{r}_2) \mathbf{r}_2^2 \Psi(\mathbf{r}_2) d\mathbf{r}_2 \right)^{1/2} \right]. \quad (8)$$

The details of the approximation as well as some evidence of the validity of the approximation are described in [30].

Thus we have to minimize (1) and (4) using various approximations for Ψ and Ψ_2 . We use the approximation $\Psi_2(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1) \Psi(\mathbf{r}_2) \mathbf{J}(\mathbf{r}_1, \mathbf{r}_2)$, where the $\mathbf{J}(\mathbf{r}_1, \mathbf{r}_2)$ is Jastrow factor [18]-[19]. But for the singlet state we can avoid the calculations of the Jastrow factor and use the simple approximation

$$\Psi_2(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_1) \Psi(\mathbf{r}_2). \quad (9)$$

III. WAVELET SCHEME

A. The numerical scheme based on wavelets

There are an infinite number of different wavelet techniques and applications [1]-[8]. We restrict our discussion to the orthonormal compact supported wavelets. Like the plane waves

in Fourier analysis wavelets are basis for expanding square-integrable function space $L^2(R)$. But unlike the harmonic functions wavelets have dual localization in both real and reciprocal spaces. Since several methods for constructing the wavelets are well documented in literature [1]- [8], we have briefly outlined the wavelet properties in Appendix A.

Any square integrable function $f(r)$ can be expanded as a sum of linear combinations of the scaling functions at chosen resolutions $j = j_0$ and wavelet functions at all finer resolutions $j \geq j_0$, i.e.

$$f(r) = \sum_s a_{j_0s} \varphi_{j_0s}(r) + \sum_{j_0}^{\infty} \sum_s d_{js} \psi_{js}(r), \quad (10)$$

where the coefficients $\{a_{j_0s}\}$ and $\{d_{js}\}$ are obtained by the scalar product with appropriate basis functions:

$$a_{j_0s} = \int f(r) \varphi_{j_0s}(r) dr, \quad d_{js} = \int f(r) \psi_{js}(r) dr. \quad (11)$$

In expansion (10) the first term gives a "coarse" approximation of $f(r)$ at the resolution j_0 , while the second term gives a sequence of successive details. In practice we actually do not use the infinite resolution therefore the sequence of details are cut off in an appropriate resolution j_{\max} . Since all the functions used in calculations are given in a finite interval, the sequence of different translates $\{s_i\}$ has also finite number S of terms in the expansion. It should be mentioned that in practice the number S can be different for coarse and fine parts of the solution. We can avoid the direct integration in numerical calculations of the coefficients (11) by using the FWT algorithm [2]. For the finite-supported wavelets the elegant pyramidal procedure can be performed, which is even faster than the Fast Fourier Transform (FFT). There is a simple rule to calculate the actual support of functions $\{\varphi_j, \psi_j\}$ in each level j in the case of an uniform mesh. The number of coefficients in dilation equations (25)-(26) is known for the concrete pair $\{\varphi, \psi\}$. Since these numbers are equal to each other for orthogonal wavelets we depict them as one symbol K . Let's discretize a function $f(r)$ on the uniform grid with steps Δr . In case of performing J -level of FWT it is convenient to believe that the coarse level j_0 is equal to zero. In this case the actual length of wavelet support L_j at level j is:

$$L_j = 2^{J-j} K \Delta r. \quad (12)$$

The multiresolution analysis with wavelets can be regarded as an additive subspace correction or as uniform mesh refinements. However, a fully refined mesh may not be necessary

to resolve the solution. Adaptive techniques have to be used to avoid this potential waste of computational efforts. The wavelet representations have a naturally built-in adaptivity through their ability to directly express and separate components living on different scales. This, combined with the fact that many operators and their inverses have nearly sparse representations in wavelet coordinates [4], [7], may eventually lead to very efficient schemes which rely on the following principle. Let us keep the computational work proportional to the number of significant coefficients in the wavelet expansion of the solution under consideration. As there are a lot of different wavelet bases with different properties (length of support, number of vanishing moments, symmetry, etc) in each case we can choose the basis which is more appropriate to the intrinsic complexity of the object under consideration. This fact makes the wavelet-based schemes to be a very sophisticated and powerful tool for compact representations of rather complex functions. For the close look to the problem we refer to the more detailed works [5]-[7].

In order to construct a complete wavelet basis set in the three-dimensional real space we employ the following approach. Let us design the 3D basis functions as a tensor product of one-dimensional wavelet functions [1], [18]. It means that in this case despite their multidimensional nature the obtained 3D-wavelet functions belong to the well defined level j . This can be achieved by taking mixed tensor products of $\varphi_{j,s}$ and $\psi_{j,s}$ which correspond in three dimensions to scaling functions,

$$\phi_{j,\mathbf{s}}(\mathbf{r}) = \varphi_{j,s_x}(r_x)\varphi_{j,s_y}(r_y)\varphi_{j,s_z}(r_z), \quad (13)$$

and seven different types of wavelets obtained by the permute multiplications:

$$\gamma_{j,\mathbf{s}}^{(1)}(\mathbf{r}) = \psi_{j,s_x}(r_x)\varphi_{j,s_y}(r_y)\varphi_{j,s_z}(r_z), \quad (14)$$

\vdots

$$\gamma_{j,\mathbf{s}}^{(4)}(\mathbf{r}) = \psi_{j,s_x}(r_x)\psi_{j,s_y}(r_y)\varphi_{j,s_z}(r_z), \quad (15)$$

\vdots

$$\gamma_{j,\mathbf{s}}^{(7)}(\mathbf{r}) = \psi_{j,s_x}(r_x)\psi_{j,s_y}(r_y)\psi_{j,s_z}(r_z). \quad (16)$$

It was shown [1] that such set was a complete basis in $L^2(R^3)$ and there were also 3D dilation equations analogous to (25) and (26) in the 1D-case [1].

For the purpose of clarity in this paper we use only the decomposition by the 3D scaling functions (13) at one initial level j_0 for the singlet bipolaron state. For more complicated

cases the terms of the wavelet decompositions (15) at more detailed levels of approximation can be added to this scheme without any sensible efforts as for example it was done in [18],[19]. As we have only one resolution level j_0 we omit this index everywhere in the following discussion. We represent the single electron wave function as:

$$\Psi(\mathbf{r}_1) = \sum_k^K A_k \phi_k(\mathbf{r}_1), \Psi(\mathbf{r}_2) = \sum_l^L B_l \phi_l(\mathbf{r}_2). \quad (17)$$

We approximate the polaron wave function as $\Psi(\mathbf{r}) = \sum_i^I P_i \phi_i(\mathbf{r})$. Following (9) it means that we can represent the two-electron wave function as:

$$\Psi_{12}(\mathbf{r}_1, \mathbf{r}_2) = \sum_k^K A_k \phi_k(\mathbf{r}_1) \sum_l^L B_l \phi_l(\mathbf{r}_2). \quad (18)$$

On the base of these representations we can find all variational terms corresponding to the variations of the equations (1) and (4) (see Appendix B). Taking into account that the first part of (6) in the bipolaron case is just proportional to the coulomb term with the coefficient $-2(1 - 1/\varepsilon)$ the total variation of the free energy functional for both polaron and bipolaron states are expressed as:

$$\begin{aligned} \frac{\delta F_p}{dP_i} &= f_p^{P_i} - \sum_k P_k L_{ik} + 2\left(1 - \frac{1}{\varepsilon}\right) P_i \sum_j C_{ij} P_j^2 \frac{V_p^{cav}}{dP_i} + 4\pi\rho k_B T P_i R_i \left(\sum_i P_j^2 R_j \right)^{1/2}, \\ \frac{\delta F_b}{dA_i} &= f_b^{A_i} - \sum_k A_k L_{ik} - A_i \sum_{jl} B_j L_{jl} B_l + 2\left(\frac{2}{\varepsilon} - 1\right) A_i \sum_j C_{ij} B_j^2 + \dots \\ &\quad \frac{1}{2} \pi \rho k_B T A_i R_i \left(\sum_j A_j^2 R_j \right)^{-1/2} \left[\left(\sum_j A_j^2 R_j \right)^{1/2} + \left(\sum_k B_k^2 R_k \right)^{1/2} \right]^2, \\ \frac{\delta F_b}{dB_i} &= f_b^{B_i} - \sum_k B_k L_{ik} - B_i \sum_{jl} A_j L_{jl} A_l + 2\left(\frac{2}{\varepsilon} - 1\right) B_i \sum_j C_{ij} A_j^2 + \dots \\ &\quad \frac{1}{2} \pi \rho k_B T B_i R_i \left(\sum_j B_j^2 R_j \right)^{-1/2} \left[\left(\sum_j A_j^2 R_j \right)^{1/2} + \left(\sum_k B_k^2 R_k \right)^{1/2} \right]^2, \end{aligned} \quad (19)$$

To find the minimum of the free energy we should equal to zero all these variations, so we obtain a set of nonlinear equations for the polaron and bipolaron respectively:

$$f_p^{\mathbf{P}} = 0, \quad f_b^{\mathbf{A}} = 0, \quad f_b^{\mathbf{B}} = 0. \quad (20)$$

These systems can be solved iteratively by the conventional numerical methods of nonlinear algebraic equations [42].

B. Details of numerical calculations

Concerning the choice of the wavelet basis set, we note that there are a lot of sets such as Daubechies, Coifman, Symlets wavelets, etc to realize the tensor orthogonal 3DFWT [1], [6]–[8]. In general the orthogonal discrete wavelet bases have not analytic expressions and hence are specified numerically and with any desirable accuracy [1]. We have chosen the Coifman 2 ($C2$) basis set [1] taking into account the following objectives. The main feature of the Coifman wavelet family is that the scaling function $\varphi(r)$ has the maximum number of vanishing moments at the fixed support. The larger is the number, the better is the approximation for singular points of the studied function [1]. Hence, using the $C2$ wavelets we can treat accurately sharp peaks of approximated functions. At the same time, the $C2$ wavelets are rather smooth to approximate the functions within the ranges between these peaks. In addition the $C2$ set is more symmetric than widely used Daubechies wavelets with the comparable support size. Nevertheless the question what kind of wavelets can be optimal has not been clarified so far. Since our procedure is based on the convenient FWT with symmetric boundary conditions [2], and on convenient calculations of simple Laplacian overlap integrals (LOI) as well as Coulomb overlap integrals (COI) (see [4],[18],[19]) only the coefficients of the corresponding wavelet filters should be replaced to perform the change of the basis set. It makes possible to perform the following pursuit of the optimal basis without serious changes in the algorithm.

In general, set (20) can be solved iteratively by the simple Picard method of direct iterations [42]. But to speed up the convergence of the numerical scheme we used the conventional Newton-Raphson procedure[42]. In the bipolaron case the Jacoby matrix \mathbf{J} is the block matrix:

$$\mathbf{J} = \begin{vmatrix} J^{AA} & J^{AB} \\ J^{BA} & J^{BB} \end{vmatrix}, \quad (21)$$

which elements are given as due to the diagonal symmetry of the matrices L_{mn} and C_{mn}

$$J_{mn}^{AA} = \frac{df_m^A}{dA_n}, \quad J_{mn}^{AB} = \frac{df_m^A}{dB_n}, \quad J_{mn}^{BA} = \frac{df_m^B}{dA_n}, \quad J_{mn}^{BB} = \frac{df_m^B}{dB_n}. \quad (22)$$

The precision parameter for the numerical solution was equal to 10^{-5} . We achieved this accuracy after 7 steps for the polaron state and 11 steps for the bipolaron state starting from the uniform density.

IV. RESULTS AND DISCUSSION

Initially we have found the suitable level of resolution. We decomposed the gaussian representation [29]-[30] of the bipolaron wave function by the 3D C2 scaling functions with different resolutions and calculated the relative difference between the total energy of this solution and 3D wavelet ones. The obtained results are presented on Fig 1. As it is seen, the accuracy is tuned exponentially with the resolution. On the other hand the increasing of resolution demands also an exponential increase of the number of wavelet coefficients. As a result, we have chosen the resolution level which corresponds to the wavelets generated on the cubic Cartesian grid with the step 1 a.u. The coordinate zero-point was in the center of the cube. In this case the number of coefficients required for polaron state is equal to 35 and 125 for the bipolaron state with the relative error about 1 % in calculations of free energy.

Another way to check the approximation quality of this decomposition by the 3D scaling functions is to consider the Pekar limit of the free energy corresponding to zero temperature. It means that we should only "switch off" the cavity contribution for the polaron. In this case there are virial relations for different free energy contributions, i.e., $F_p : |T_p| : V_{ex} = 1 : 1 : 2$ [46]. We have obtained $F_p : |T_p| : V_{ex} = 1 : 1.002 : 2.002$ in our calculations that indicates that the accuracy of the virial relations lies in the range of 0.5%. On the other hand using the wavelet approximation we have obtained the polaron free energy in the Pekar limit near to 0.5% error of the best estimated value [47].

It should be mentioned also that due to the sophisticated choice of the basis set, the level of resolution and the number of basis function we obtain the computational cost only 3 times higher as compared with our previous work which was based on the 1D wavelets. The main reason is that our scheme uses the operator representations which are very sparse diagonal. For example for Laplacian term we should calculate the only axes-liked values (see Appendix B). In addition due to the exponential decay of these operators (see Fig 2.) we can neglect also most of all the non-zero values.

We have calculated the free energy and mean radius for the polaron and bipolaron formations in two different liquids: water at 300 K (dielectric constant is equal to 78) and liquid ammonium at 100 K (dielectric constant is equal to 20). The results are in Table 1, which includes the free energy of two polarons $2F_p$ and bipolaron F_b and its difference δ for water and liquid ammonia, the mean radii r_p and r_b of the polaron and bipolaron correspondingly.

For convenience the energy parameters are presented in eV and mean radii are presented in Angstroems. We can see that both states are stable under these conditions. But if we compare the difference between the free energy of the bipolaron formation and that of two separate polarons we recognize that in liquid ammonia the bipolaron state is more preferable and on the contrary in water the polaron state is little bit more stable. These data are in agreement with the experimental results (see discussion in [29]).

Our study indicates that the discrete wavelets are a suitable and powerful instrument to approximate 3D wave functions of mixed quantum-classical systems. The applied scheme of the 3D wavelet approximation allows us to describe the complete 3D structure of quantum complexes with a small number of approximating coefficients. It can be a reliable base for future theoretical investigations of more complex quantum-classical systems. The following task is to avoid the simplification (6) - (7) and apply the 3D wavelet scheme for calculation of the solvent structure relying on the hybrid DFT algorithm based 1D wavelets [40]. It will allow us to build a numerical scheme which would be as realistic as MD/MC simulations without huge computational costs. The application of DFT to molecular liquids [43]-[45] indicates that the method is very promising to treat solvation phenomena. The next task is to apply our model to the investigation of the bipolaron triplet state formation. In this case the wave functions are not spherically symmetrical, however the 3D wavelet approach will be an effective tool to treat this problem. We suppose that the wavelet study can provide further progress in this direction.

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Appendix A

The wavelet functions generate in $L^2(R)$ a hierarchical sequence of subspaces which forms the multiresolution analysis (MRA). The scaling function $\varphi(r)$ generates a MRA if it satisfies the following conditions:

i) translates $\varphi_s = \varphi(r - s)$ are linearly independent and produce an orthonormal basis of the subspace $V_0 \subset L^2(R)$, $s \in Z$;

ii) dilates $\varphi_{js} = \varphi(2^j r - s)$ generate subspaces V_j , $j \in Z$, so that

$$\dots \subset V_{-1} \subset V_0 \subset V_1 \subset \dots \subset V_j \subset \dots, \quad \bigcup_{j=-\infty}^{\infty} V_j \text{ is dense in } L^2, \quad \bigcap_{j=-\infty}^{\infty} V_j = 0, \quad (23)$$

iii) there is such a wavelet function that its translates $\psi_s = \psi(r - s)$ are linearly independent and produce an orthonormal basis of the subspace W_0 which is complimentary to V_0 so that $V_1 = V_0 \oplus W_0$. From the above relations it follows that $L^2(R)$ can be decomposed to the approximation space V_{j_0} and the sum of the detailed spaces W_j of higher resolution:

$$L^2(R) = V_{j_0} \oplus \bigoplus_{j \geq j_0}^{\infty} W_j, \quad (24)$$

where the $j_0 \in Z$ is a closed level of resolution. From Eq. (23) it is also follows that all $\{\psi_{js} = \psi(2^j r - s), \quad j, s \in Z\}$ constrain an orthonormal basis of $L^2(R)$.

As $\varphi(r) \subset V_0$ and $V_0 \subset V_1$ we can express $\varphi(r)$ in terms of basis function of V_1 :

$$\varphi(r) = \sum_s h_s \varphi(2r - s). \quad (25)$$

The equation is called a dilation equation. Similarly, $\psi(r)$ must satisfy a wavelet dilation equation:

$$\psi(r) = \sum_s w_s \psi(2r - s). \quad (26)$$

The scaling function and the wavelet have finite support if and only in the case of the finite number of coefficients h_s and w_s . The functions $\varphi(r)$ and $\psi(r)$ have also the properties:

$$\begin{aligned} \int \varphi(r) dr &= 1; & \int \psi(r) dr &= 0; \\ \int \varphi_{ja}(r) \varphi_{jb}(r) dr &= \delta_{ab}; & \int \psi_{ja}(r) \psi_{kb}(r) dr &= \delta_{jk} \delta_{ab}; & \int \varphi_{ja}(r) \psi_{jb}(r) dr &= 0. \end{aligned} \quad (27)$$

Appendix B

The variation δT of the kinetic energy term in (1) by vector \mathbf{P} of the expansion coefficients $\{P_k\}$ is

$$\delta T_p = -d\mathbf{P} \int d\mathbf{r} \sum_k^K P_k \phi_k(\mathbf{r}) \nabla^2 \sum_n^N \phi_n(\mathbf{r}). \quad (28)$$

and correspondingly the variations δT_1 and δT_2 of the kinetic term for bipolaron are:

$$\begin{aligned}
\delta T_1 &= -d\mathbf{A} \int d\mathbf{r}_1 \sum_k^K A_k \phi_k(\mathbf{r}_1) \nabla_1^2 \sum_n^N \phi_n(\mathbf{r}_1) \int d\mathbf{r}_2 \sum_l^L B_l \phi_l(\mathbf{r}_2) \sum_m^M B_m \phi_m(\mathbf{r}_2) - \dots \\
&\quad d\mathbf{B} \int d\mathbf{r}_1 \sum_k^K A_k \phi_k(\mathbf{r}_1) \nabla_1^2 \sum_n^N A_n \phi_n(\mathbf{r}_1) \int d\mathbf{r}_2 \sum_l^L B_l \phi_l(\mathbf{r}_2) \sum_m^M \phi_m(\mathbf{r}_2), \quad (29) \\
\delta T_2 &= -d\mathbf{A} \int d\mathbf{r}_1 \sum_k^K A_k \phi_k(\mathbf{r}_1) \sum_n^N \phi_n(\mathbf{r}_1) \int d\mathbf{r}_2 \sum_l^L B_l \phi_l(\mathbf{r}_2) \nabla_2^2 \sum_m^M B_m \phi_m(\mathbf{r}_2) - \dots \\
&\quad d\mathbf{B} \int d\mathbf{r}_1 \sum_k^K A_k \phi_k(\mathbf{r}_1) \sum_n^N A_n \phi_n(\mathbf{r}_1) \int d\mathbf{r}_2 \sum_l^L B_l \phi_l(\mathbf{r}_2) \nabla_2^2 \sum_m^M \phi_m(\mathbf{r}_2).
\end{aligned}$$

Due to the orthogonality of the scaling functions the overlap integral $\int d\mathbf{r} \phi_i(\mathbf{r}) \phi_j(\mathbf{r})$ is equal to δ_{ij} . Following identities (27) and the fact that the wave functions are normalized we obtain $\sum_i P_i^2 = \sum_k A_k^2 = \sum_l B_l^2 \equiv 1$, and rewrite (28) and (29) as:

$$\frac{dT_p}{dP_i} = - \sum_k P_k L_{ik}, \quad (30)$$

$$\frac{dT_b}{dA_i} = - \sum_k A_k L_{ik} - A_i \sum_{jl} B_j L_{jl} B_l, \quad \frac{dT_b}{dB_i} = - \sum_k B_k L_{ik} - B_i \sum_{jl} A_j L_{jl} A_l, \quad (31)$$

where the terms L_{ij} are referred to as the Laplacian Overlap Integrals (LOI)

$$L_{ik} = \int d\mathbf{r} \phi_i(\mathbf{r}) \nabla^2 \phi_k(\mathbf{r}). \quad (32)$$

In our case due to the orthogonality of one-dimensional components of the multidimensional tensor-product wavelets the LOI are:

$$\begin{aligned}
L_{ij} &= \delta_{i_y k_y} \delta_{i_z k_z} \int dr_x \varphi_{i_x}(r_x) \nabla_x^2 \varphi_{k_x}(r_x) + \delta_{i_x k_x} \delta_{i_z k_z} \int dr_y \varphi_{i_y}(r_y) \nabla_y^2 \varphi_{k_y}(r_y) + \dots \quad (33) \\
&\quad + \delta_{i_x k_x} \delta_{i_y k_y} \int dr_z \varphi_{i_z}(r_z) \nabla_z^2 \varphi_{k_z}(r_z).
\end{aligned}$$

Thus the problem is reduced to the calculation of small number of 1D overlap integrals. It can be iteratively done with any accuracy by several ways (see [4], [1],[18]. The variations of these terms in these polaron and bipolaron cases are:

$$\delta V_p^c = 2\left(1 - \frac{1}{\varepsilon}\right) d\mathbf{P} \int \int d\mathbf{r} d\mathbf{r}' \frac{\left(\sum_k^K P_k \phi_k(\mathbf{r}) \sum_l^L \phi_l(\mathbf{r})\right) \left(\sum_m^M P_m \phi_m(\mathbf{r}')\right)^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (34)$$

$$\begin{aligned} \delta V_b^c = & 2d\mathbf{A} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\sum_k^K A_k \phi_k(\mathbf{r}_1) \sum_l^L \phi_l(\mathbf{r}_1) (\sum_m^M B_m \phi_m(\mathbf{r}_2))^2}{|\mathbf{r} - \mathbf{r}'|} + \\ & 2d\mathbf{B} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{(\sum_k^K A_k \phi_k(\mathbf{r}_1))^2 \sum_m^M B_m \phi_m(\mathbf{r}_1) \sum_n^N \phi_n(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \end{aligned} \quad (35)$$

These integrals can be expressed via the elementary coulomb overlap integrals (COI):

$$C_{ikjl} = \int \int d\mathbf{r} d\mathbf{r}' \phi_i(\mathbf{r}) \phi_k(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_j(\mathbf{r}') \phi_l(\mathbf{r}'). \quad (36)$$

In the case of orthogonal Coifman wavelets these terms can be well approximated with the minimal error [4] as:

$$C_{ikjl} \cong \delta_{ij} \delta_{kn} C_{ikjl} = C_{ij} = C_{0(j-i)} = \int \int d\mathbf{r} d\mathbf{r}' \phi_0(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \phi_{j-i}(\mathbf{r}'). \quad (37)$$

These integrals can be calculated iteratively with any desirable accuracy as described in [18].

Thus we obtain:

$$\frac{\delta V_p^c}{dP_i} = 2(1 - \frac{1}{\varepsilon}) P_i \sum_j C_{ij} P_j^2, \quad \frac{\delta V_b^c}{dA_i} = 2A_i \sum_j C_{ij} B_j^2, \quad \frac{\delta V_b^c}{dB_i} = 2B_j \sum_i C_{ij} A_i^2. \quad (38)$$

For the orthogonal Coifman basis the integrals (3) and (8) can be well approximated via the integrals R_{ij} :

$$R_{ij} = \int \phi_i(\mathbf{r}) \mathbf{r}^2 \phi_j(\mathbf{r}) d\mathbf{r} \cong \delta_{ij} \int \phi_i(\mathbf{r}) \mathbf{r}^2 \phi_j(\mathbf{r}) d\mathbf{r}. \quad (39)$$

Thus, the variations of the cavity formation energy can be expressed for the polaron and bipolaron cases as:

$$\begin{aligned} \frac{V_p^{cav}}{dP_i} &= 4\pi\rho k_B T P_i R_i \left(\sum_i P_j^2 R_j \right)^{1/2}, \\ \frac{V_b^{cav}}{dA_i} &= \frac{1}{2} \pi \rho k_B T A_i R_i \left(\sum_j A_j^2 R_j \right)^{-1/2} \left[\left(\sum_j A_j^2 R_j \right)^{1/2} + \left(\sum_k B_k^2 R_k \right)^{1/2} \right]^2, \\ \frac{V_b^{cav}}{dB_i} &= \frac{1}{2} \pi \rho k_B T B_i R_i \left(\sum_j B_j R_j \right)^{-1/2} \left[\left(\sum_j A_j R_j \right)^{1/2} + \left(\sum_k B_k R_k \right)^{1/2} \right]^2. \end{aligned} \quad (40)$$

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Table 1. Parameters of polaron and singlet bipolaron in water and liquid ammonium.

	$2F_p(eV)$	$F_b(eV)$	$\delta(eV)$	$r_p(\text{\AA})$	$r_b(\text{\AA})$
Water	-1.31	-1.20	0.11	2.3	2.8
Ammonium	-1.22	-1.58	-0.35	2.9	3.5

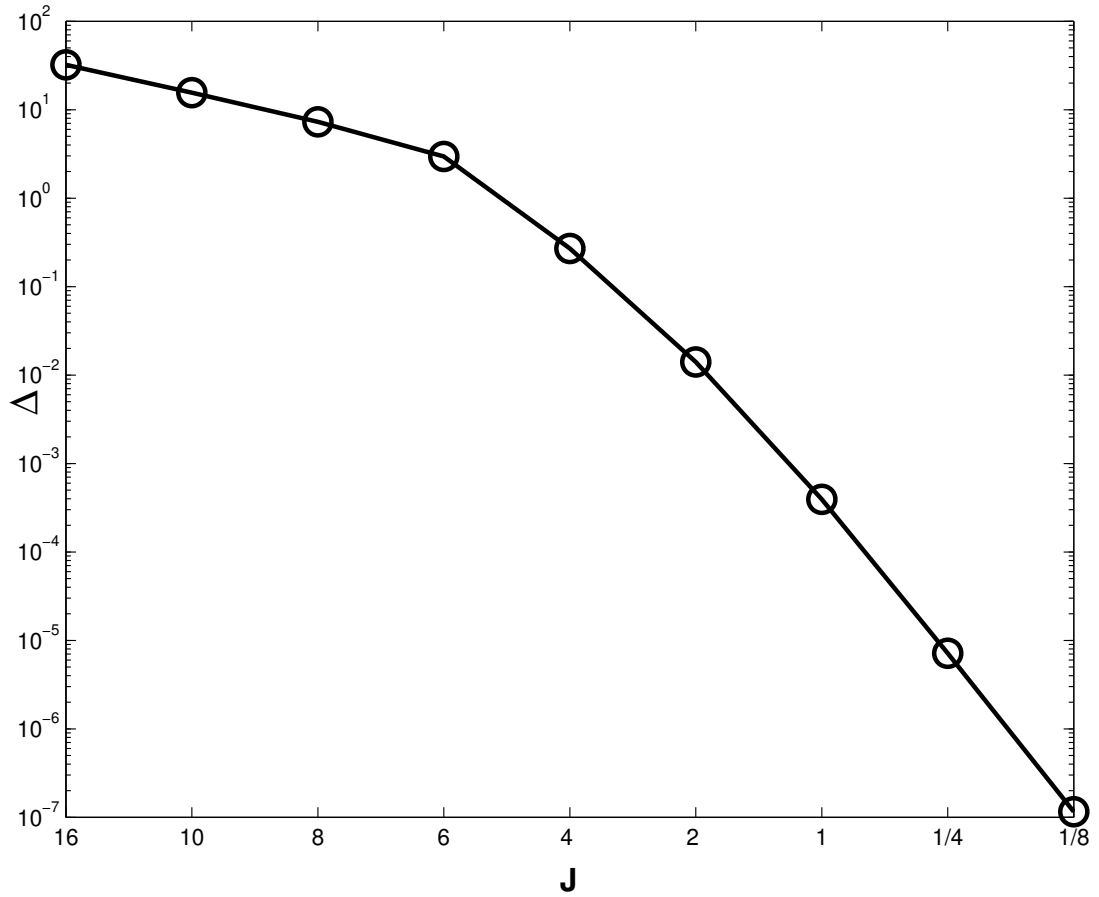


FIG. 1: The dependence of relative error in free energy on the resolution of the wavelet transform. The error was calculated with comparison to the Gaussian solution for the bipolaron [30].

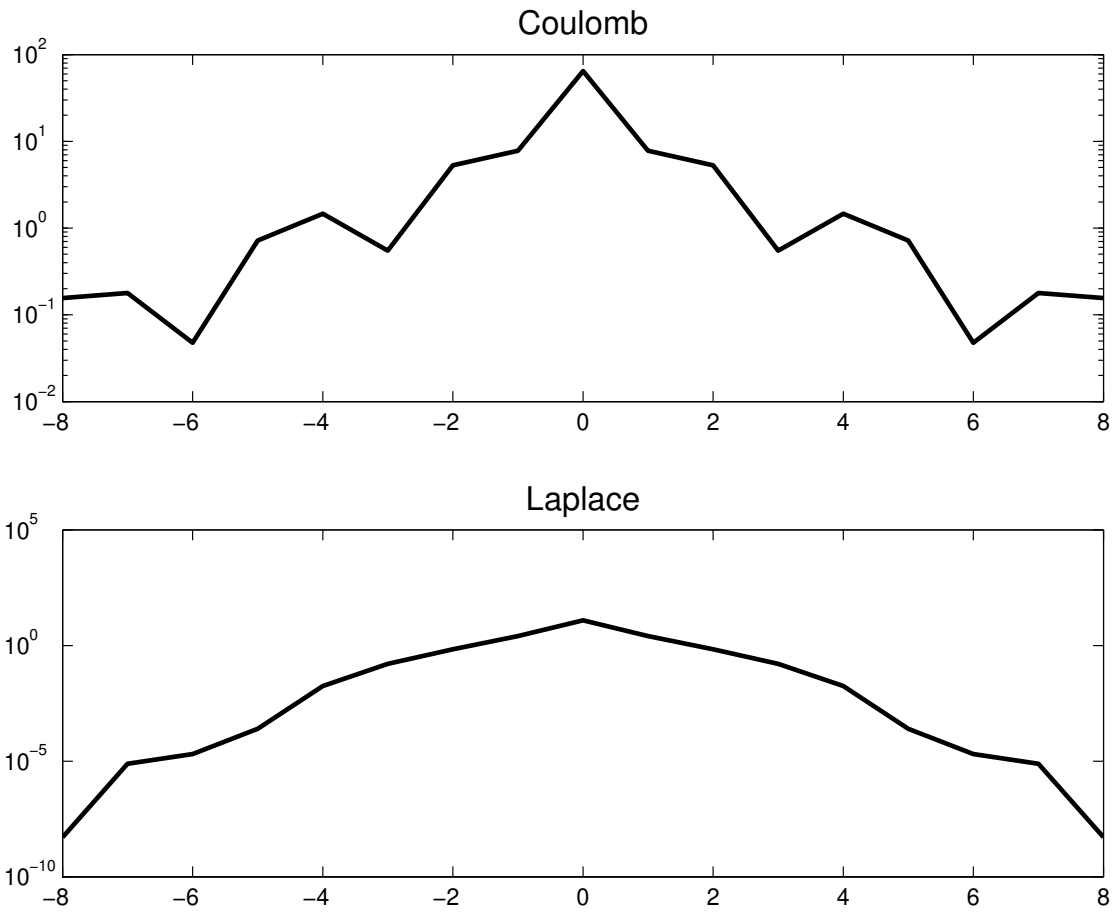


FIG. 2: The absolute values of radial part of the Coulomb Overlap Integrals (top) and Laplace Overlap Integrals (bottom). The values on the ordinate axis are in the logarithmic scales.