

An ab-initio Computational Method to Determine Dielectric Properties of Biological Materials

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Supplementary Materials

Theory: Density Functional Theory (DFT) and Molecular Dynamics (MD)

Density functional theory or molecular dynamics simulation methods can be used to model atomic or molecular models and this provide information such as dipolar moment and polarizability of the model. In three dimension computer simulations of small number of molecules, the density fluctuates tremendously near the boundary destroying dielectric properties [18]. This can be overcome by using boundary conditions and continuum models where a modified dipole-dipole interaction is used instead of true interaction [18].

Thus, the dielectric constant of the system becomes a function of modified dipole-dipole tensor. One way to modify dipolar interactions is to use a reaction field where the sample is embedded in a dielectric continuum. The continuum is polarized by the arrangement of molecular dipoles producing an additional electric field called reaction field. In reaction field, the interactions of more distant molecules (distance between two molecules i and j , $r_{ij} > r_c$, cutoff radius) are neglected and replaced by a continuum with dielectric constant ϵ_{RF} [19]. This external dielectric constant ϵ_{RF} is given by $2(\epsilon_{RF} - 1)/(2\epsilon_{RF} + 1)I = \lim_{r_0 \rightarrow \infty} \{ (3/4\pi) \int T_{mod}(r) dr \}$ where T_{mod} is the modified dipole-dipole tensor. The static dielectric constant of the system depends on the dielectric constant of the continuum which is used in the simulation. This varies

with molecule type and volume (number of molecules of the system). The value for ϵ_{RF} to be used in the

simulation ϵ_{RF}' ($\epsilon_{RF}' < \epsilon_{RF}$) can be found by $\frac{2(\epsilon_{RF}' - 1)}{2\epsilon_{RF}' + 1} \frac{4\pi/3}{\int_{r < r_c} dr f(r)} = \frac{2(\epsilon_{RF} - 1)}{2\epsilon_{RF} + 1} \frac{1}{r_c^3}$ where $f(r)$ is a

smoothing function [19].

The dielectric properties of clusters depend on both dipole moment and polarizability of the individual molecules. The effective permanent dipole moment depends on molecular properties, temperature and density of the liquid [19]. The dipole moment of molecule i is the sum of the permanent and induced moments, $m_i = \mu_i + p_i$. The induced dipole moment is $p_i = \alpha E_i$, which is due to the linear polarization and isotropic point polarizability α , where E_i is the local electric field at i due to the charge sites on all the other molecules [20]. Thus, the average dipole moment of the molecular system is $\langle m \rangle = \mu + \alpha \langle E \rangle$. If N particles with molecular dipole moment μ in a volume V (volume of the system) at temperature T (Kelvin) are considered, the static dielectric constant can be calculated from the fluctuations in the total dipole moment as,

$$\frac{4\pi}{3} \frac{(\langle M^2 \rangle - \langle M \rangle^2)}{Vk_b T \epsilon_a} = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_{RF} + 1)}{(2\epsilon_{RF} + \epsilon_0)} \quad (2)$$

where $M(t) = \sum \mu_i(t)$ is the total dipole moment of the system, ϵ_∞ is the dielectric constants at infinite frequencies, V is the volume of the system, k_b is the Boltzmann constant, T is the temperature in Kelvin, ϵ_a is the permittivity of vacuum, ϵ_0 is the static dielectric constant, and ϵ_{RF} is the dielectric constant of the continuum [19, 21]. Since, the dipole moment is a vector, the fluctuations are given by $(\langle M^2 \rangle - \langle M \rangle^2) = \langle M_x^2 + M_y^2 + M_z^2 \rangle - (\langle M_x \rangle + \langle M_y \rangle + \langle M_z \rangle)^2$ where M_x , M_y and M_z are the total dipole moments in x , y and z directions.

The dielectric constant at infinite frequency is calculated using the polarizability α of the model as,

$$\frac{4\pi\alpha}{V} = \frac{(\epsilon_\infty - 1)(2\epsilon_{RF} + 1)}{(2\epsilon_{RF} + \epsilon_\infty)} \quad (3)$$

where the mean polarizability $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ is the trace of the polarizability tensor, and α_{xx} , α_{yy} , and α_{zz} are the polarizability in xx , yy and zz directions respectively. The frequency dependent permittivity is calculated using Fourier-Laplace transform ($L_{i\omega}$) of normalized autocorrelation function of the total dipole moment $\phi(t) = \langle M(0)M(t) \rangle / \langle M(0)^2 \rangle$ [21], where, $L_{i\omega}[-\phi] = (\varepsilon(\omega) - \varepsilon_\infty)(2\varepsilon_{RF} + \varepsilon_0) / (\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_{RF} + \varepsilon(\omega))$. Assuming that the system behaves like a Debye dielectric, the normalized autocorrelation function can be written as $\phi(t) = \exp(-t/\tau)$, where

$$\tau_D = \tau \frac{(2\varepsilon_{RF} + \varepsilon_0)}{(2\varepsilon_{RF} + \varepsilon_\infty)} \quad (4)$$

and τ_D is the Debye relaxation time. Thus, the frequency dependent permittivity is given by the Debye model as $\varepsilon(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/(1 + i\omega\tau_D)$ [22].

Polarizability from Density Functional Theory (DFT)

Here, the static polarizability values obtained from local density approximations (LDA) and generalized gradient approximations (GGA) were compared using the exchange-correlation functional implemented in deMon2k. The polarizability values of water and methanol clusters obtained from VWN exchange-correlation functional (Local Vosko, Wilk and Nusair correlation) which is based on LDA, PW86 (PW86 GGA exchange with P86 GGA correlation), BLYP (B88 GGA exchange with LYP GGA correlation), OLYP (HC01 GGA exchange with LYP GGA correlation) and PW91 (PW91 GGA exchange and correlation) which are based on GGA were compared with the results presented in [8] and [9]. The polarizability of water clusters were obtained using Hartree-Fock (HF) levels and 6-31++G(d,p) basis set in [8], and the polarizability of methanol clusters were calculated using B3LYP/6-31++G(d,p) method in [9]. Figures S1 and S2 show the error percentage of calculating the polarizability values obtained from LDA and GGA compared with the values in [8] and [9]. The experimentally obtained polarizability values of neo-pentane and propane are 69 and 42.4 [10] and these values were computed using LDA to

within 10 % error and GGA within to 16 % error. Thus in this study, static polarizability values used to calculate the dielectric constant at infinite frequency were obtained from VWN which is based on LDA.

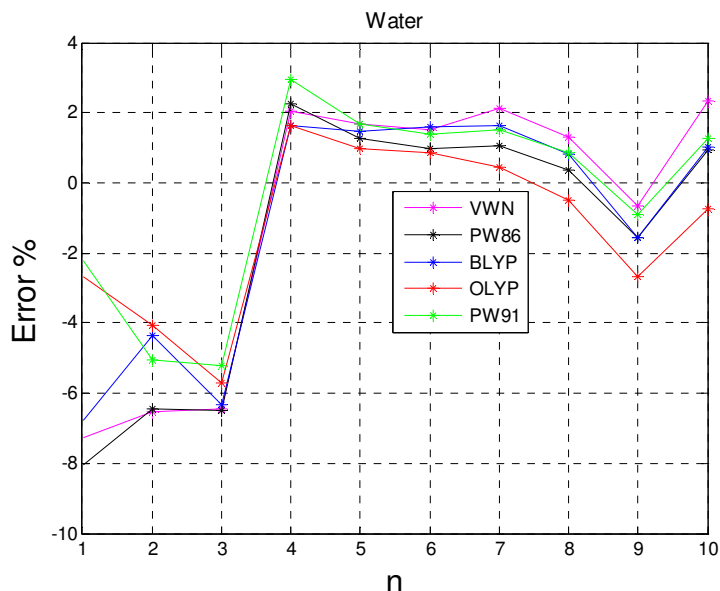


Fig. S1: A comparison of the polarizability values of water clusters obtained from GGA and LDA with the results presented in [8]. In [8], the polarizability of water clusters were obtained using Hartree-Fock (HF) levels and 6-31++G(d,p) basis set.

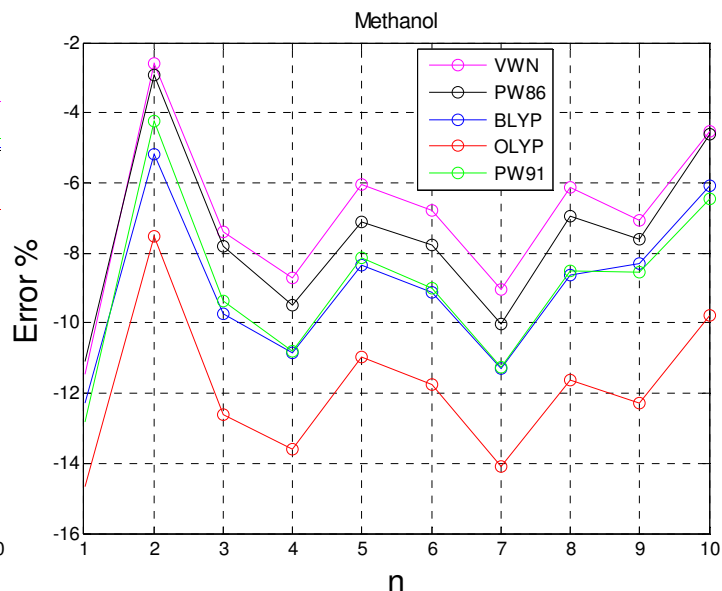


Fig. S2: A comparison of the polarizability values of methanol clusters obtained from GGA and LDA with the results presented in [9]. In [9], the polarizability of methanol clusters were calculated using B3LYP/6-31++G(d,p) method.

Structure of Bio-molecules Used in Molecular Dynamics Simulations

In this study, aqueous solutions of amino acids and neurotransmitters were created by adding water molecules as specified in Table 3 to four molecules of amino acids and neurotransmitters, respectively. The molecular structures (orientation of molecules and the distance between molecules) of amino acids and neurotransmitters are shown in Figures S3 - S7.

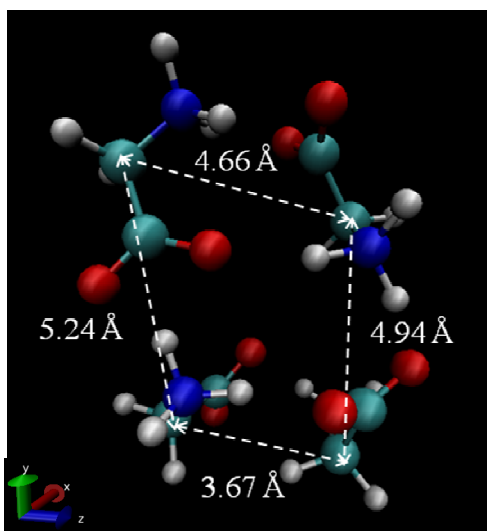


Fig. S3: The orientation of glycine molecules in glycine 1 M aqueous solution that result in $\epsilon_0 = 97.36 \pm 4$, and $\tau_D = 20.81 \pm 2.6$ ps.

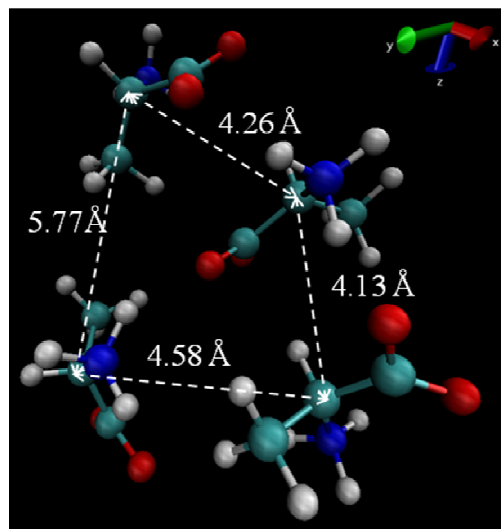


Fig. S4: The orientation of alanine molecules in alanine 1 M aqueous solution that result in $\epsilon_0 = 89.52 \pm 3$, and $\tau_D = 33 \pm 2.5$ ps.

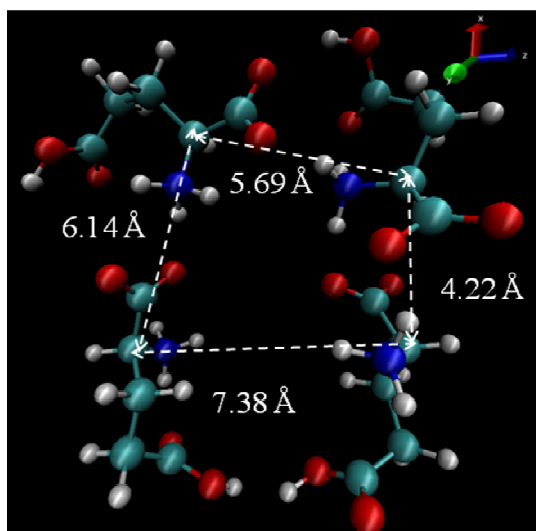


Fig. S5: The orientation of glutamic molecules in glutamic 1 M aqueous solution that result in $\epsilon_0 = 110.21 \pm 4$, and $\tau_D = 152.43 \pm 3$ ps.

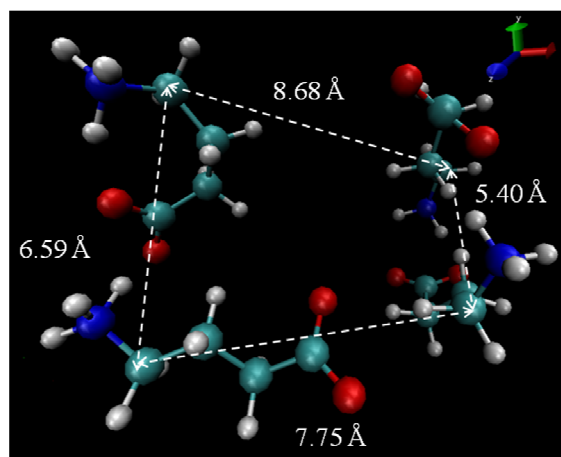


Fig. S6: The orientation of gaba molecules in gaba 1 M aqueous that result in $\epsilon_0 = 120.72 \pm 2$, and $\tau_D = 126.55 \pm 2.6$ ps.

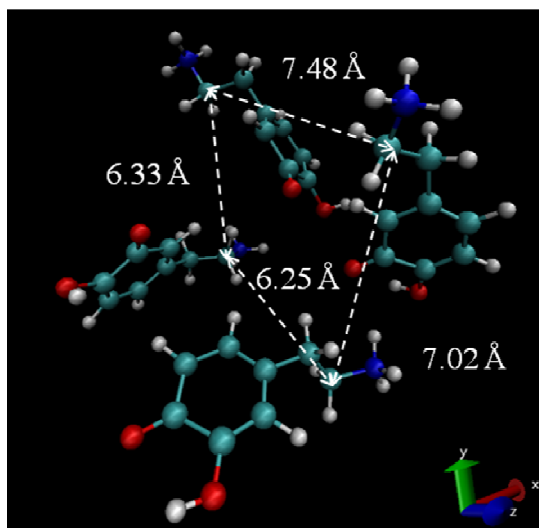


Fig. S7: The orientation of dopamine molecules in dopamine 1 M aqueous solution that result in $\epsilon_0 = 102.7 \pm 4$, and $\tau_D = 137.52 \pm 5$ ps.

References

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