Supporting Information Available

Valentina Tozzini

NEST - Scuola Normale Superiore, Piazza dei Cavalieri, 7 I-56126 Pisa, Italy

Walter Rocchia

Scuola Normale Superiore, Piazza dei Cavalieri, 7 I-56126 Pisa, Italy

J. Andrew McCammon

Department of Chemistry and Biochemistry, Center for Theoretical Biological Physics, Howard Hughes Medical Institute, Department of Pharmacology University of California at San Diego, La Jolla, California 92093, USA

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1 Derivation of the exact formula for $\alpha(\phi, \psi)$

The general formula for $\alpha(\phi, \psi)$ depends on four variables, namely $(\phi_i, \phi_{i+1}, \psi_i, \psi_{i+1})$. The expression for $\tan(\alpha)$ is a rational function of fourth order trigonometric polynomials in the mentioned variables. Each coefficient is, in turn, a polynomial in $\sin(\gamma 1)$, $\cos(\gamma 1)$, $\sin(\gamma 2)$, $\cos(\gamma 2)$, $\sin(\tau)$ and $\cos(\tau)$. The whole exact, symbolic, expression contains hundreds of terms, and is definitely not manageable. However, by substituting the numerical values of the parameters namely $\gamma 1 = 20.7$ deg, $\gamma 2 = 14.7$ deg and $\tau = 111$ deg, one can obtain a numerical expression (that we called "actual") that is implementable in a computer code.

In the approximation $\phi_i = \phi_{i+1}$ and $\psi_i = \psi_{i+1}$ a manageable expression can be obtained at the second order in γ_1, γ_2 and $\tau - \pi/2$:

$$\alpha = \phi + \psi + \pi + \gamma 1 \sin(\psi) + \gamma 2 \sin(\phi) + \frac{1}{4}\gamma 1^2 \sin(2\psi) + \frac{1}{4}\gamma 2^2 \sin(2\phi) + \gamma 1 \gamma 2 \sin(\phi + \psi) \\ -\gamma 1(\tau - \pi/2)\sin(\psi) - \gamma 2(\tau - \pi/2)\sin(\phi)$$

Careful attention needs to be paid to keep the value of alpha in the $[-\pi; \pi]$ interval. We observe that $\tau - \pi/2$ appears only in the second order mixed terms, coupled with $\gamma 1$ and $\gamma 2$. In its linear approximation, this expression returns eqn. (2) (see main text), where the dependence on τ is absent.

In fig. 1, we compare the performance of the second order formula and the first order formula plotting the approximate values of α versus the "actual" ones. As can be seen from the graphs, the second order formula is an excellent approximation of the desired value for α, (relative error of $\sim$1.4%, on a suitably populated configurational ensemble). However, the first order formula can also be a good approximation, if the values of the parameters are "optimized" to reproduce the true values. Using the optimized values of the parameters, we obtain, on the same ensemble, a relative error of $\sim$3.7%.

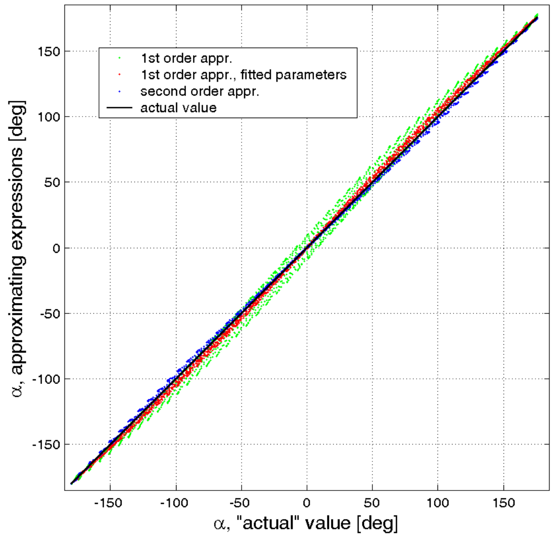

Figure 1: Approximate values of α versus the exact ones, evaluated on a set of ϕ, ψ pairs evenly spaced in the ϕ, ψ plane. Black line: explicit numeric formula, used as reference. Blue line: second order formula, using the actual values of the parameters: $\gamma 1 = 20.7$ deg, $\gamma 2 = 14.7$ deg, $\tau = 111$ deg. Green line: first order formula using the actual values of the parameters. Red line: first order formula, using optimized values of the parameters, $\gamma 1 = 15$ deg, $\gamma 2 = 20$ deg