Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Long-range electron-electron interaction and charge transfer in protein complexes: a numerical approach

Supporting information

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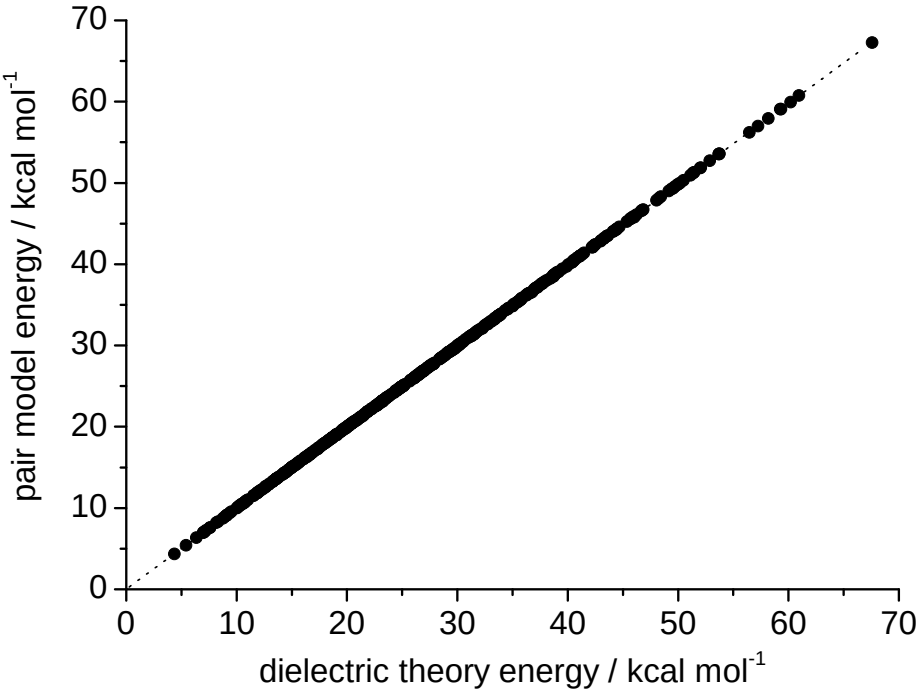
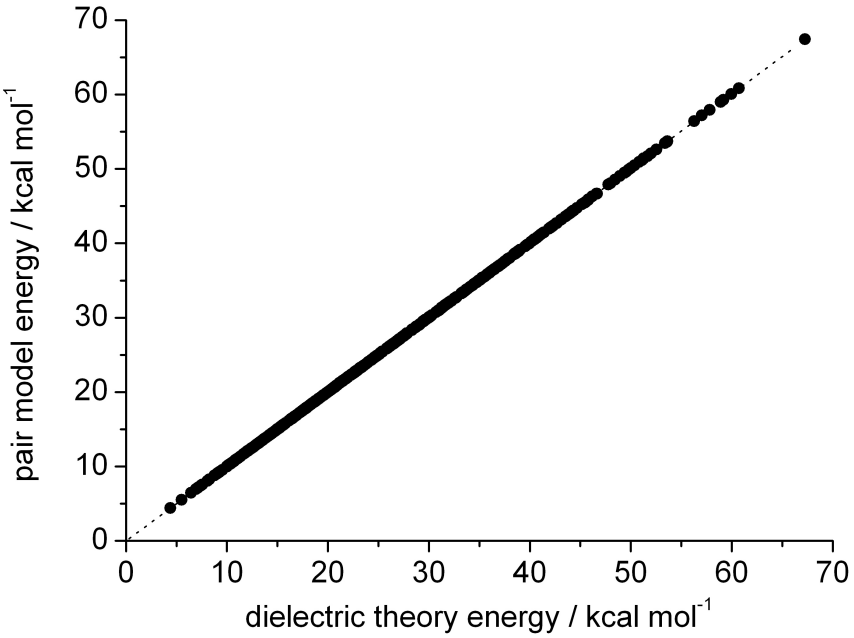
Pair model verification



Test of the pair model in the absence of an electrolyte. Pair model energies as a function of the reference dielectric theory model. Data as filled circles (•), dotted regression line. All energies in kcal/mol. As regression data, we have an energy offset of 0.026 ± 0.004 kcal/mol, a slope of 0.9963 ± 0.0001, and a squared regression coefficient R^2=0.99999214.



Test of the pair model in the presence of an electrolyte. Pair model energies as a function of the reference dielectric theory model. Data as filled circles (•), dotted regression line. All energies in kcal/mol. As regression data, we have an energy offset of -0.022 ± 0.003 kcal/mol, a slope of 1.0020 ± 0.0001, and a squared regression coefficient of R^2=0.99999660.

Alternative NrfHA charging scheme

Aufbau principle for the sequential addition of electrons to NrfHA with A1 and H1 site energies shifted by 2 kcal/mol. Number of electrons m, energies in kcal/mol relative to the zero-electron state, binary representation of the state. This representation codes the occupation of the sites A1-A2-A3-A4-A5-H1-H2-H3-H4.

m	E (kcal/mol)	occupation
1	2.41	00000 0001
2	4.77	10001 0000
3	8.41	10001 0001
4	12.78	10001 1001
5	18.49	11001 1001
6	25.51	11001 1011
7	36.22	11001 1111
8	49.90	11011 1111
9	71.43	11111 1111

$NrfHA_2$ charging scheme

Low-energy electronic configurations of the $NrfHA_2$ heterotrimer. Number of electrons m, potential energy E, partition sum z, electronic configuration. For the latter, the sites are encoded as: first five digits A1-A2-A3-A4-A5 (internal A subunit), digits six to eleven: A1-A2-A3-A4-A5 (external A subunit), last four digits: H1-H2-H3-H4 (H subunit),

m	E (kcal/mol)	z	occupation
1	-1.24	1.20	00000 00000 0001
2	-0.52	1.29	10000 00000 0001
3	1.14	1.13	10000 10000 0001
4	4.76	1.73	10001 10000 0001
	5.32		10000 10000 1001
5	9.18	2.03	10001 10000 1001
	9.46		10001 11000 0001
6	14.08	1.20	10001 11000 1001

Heme force field parameters

Entries in the last column refer to either of these works:

[Bauß 2015] A. Bauß and T. Koslowski. Storage, transport, release: heme versatility in nitrite reductase electron transfer studied by molecular dynamics simulations. *Physical Chemistry Chemical Physics* 17, 4483-4491 (2015)

[Giammona 1984] D.A. Giammona, *Examination of conformational flexibility in porphyrins and bulky-ligand binding in Myoglobin*, PhD thesis, University of California, Davis 1984.

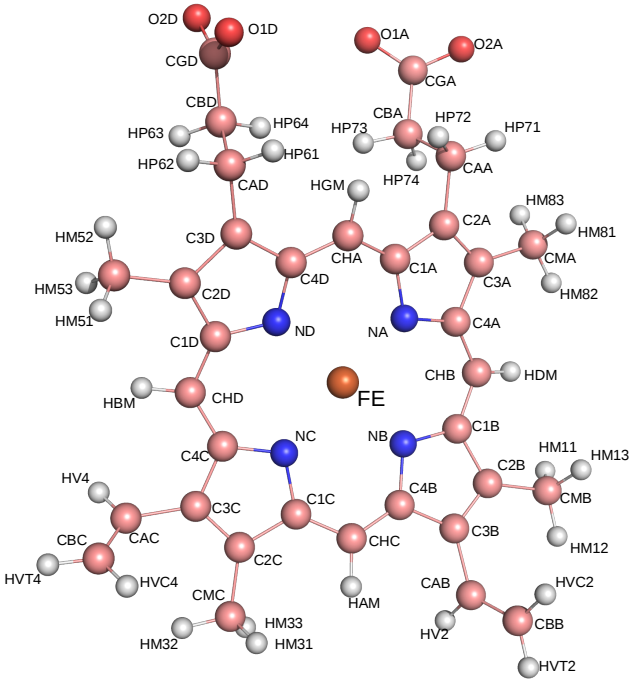
[Burggraf 2012] F. Burggraf, *Beiträge zur Theorie des Elektronentransfer in photosyntetischen Reaktionszentren von Purpurbakterien*, PhD thesis, University of Freiburg 2012.

[Tinker] L. Lagardere, L.-H. Jolly, F. Lipparini, F. Aviat, B. Stamm, Z. Jing, F. Zhifeng, M. Harger, H. Torabifard, A. Cisneros, M. Schnieders, N. Gresh, Y. Maday, P. Ren, J. Ponder, J.P. Piquemal, Tinker-HP: a Massively Parallel Molecular Dynamics Package for Multiscale Simulations of Large Complex Systems with Advanced Point Dipole Polarizable Force Fields, *Chemical Science* 9, 956972 (2018)

[Amber98] T. E. Cheatham III, P. Cieplak and P. A. Kollman, A Modified Version of the Cornell et al. Force Field with Improved Sugar Pucker Phases and Helical Repeat, *J. Biomol. Struct. Dyn.*, 16, 845-862 (1999); W. D. Cornell, P. Cieplak, C. I. Bayly, I. R. Gould, K. M. Merz, Jr., D. M. Ferguson, D. C. Spellmeyer, T. Fox, J. W. Caldwell and P. A. Kollman, A Second Gener-

ation Force Field for the Simulation of Proteins, Nucleic Acids, and Organic Molecules, *J. Am. Chem. Soc.*, 117, 5179-5197 (1995)

[Shannon1976] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallographica A* 32, 751-756 (1976)



Oxidized heme atom charges in multiples of the elementary charge.

atom	charge	source
FE	0.4473	Bauß 2015
NA	-0.2485	Bauß 2015
C1A	0.0264	Bauß 2015
C2A	0.0205	Bauß 2015
CAA	-0.1761	Bauß 2015
HP71	0.1000	Bauß 2015
HP72	0.1000	Bauß 2015
CBA	-0.3094	Bauß 2015
HP73	0.1000	Bauß 2015
HP74	0.1000	Bauß 2015
CGA	0.2925	Bauß 2015
O1A	-0.4814	Bauß 2015
O2A	-0.4773	Bauß 2015
C3A	-0.0083	Bauß 2015
CMA	-0.2200	Bauß 2015
HM81	0.0750	Bauß 2015
HM82	0.0750	Bauß 2015
HM83	0.0750	Bauß 2015
C4A	0.0639	Bauß 2015
CHB	-0.0861	Bauß 2015
HDM	0.1500	Bauß 2015
C1B	0.0425	Bauß 2015

NB	-0.0453	Bauß 2015
C2B	0.0098	Bauß 2015
CMB	-0.2136	Bauß 2015
HM11	0.0750	Bauß 2015
HM12	0.0750	Bauß 2015
HM13	0.0750	Bauß 2015
C3B	0.0751	Bauß 2015
CAB	-0.1641	Bauß 2015
HV2	0.1500	Bauß 2015
CBB	-0.2250	Bauß 2015
HVC2	0.1000	Bauß 2015
HVT2	0.1000	Bauß 2015
C4B	-0.1197	Bauß 2015
CHC	0.0221	Bauß 2015
HAM	0.1500	Bauß 2015
C1C	-0.0383	Bauß 2015
NC	-0.1668	Bauß 2015
C2C	0.0054	Bauß 2015
CMC	-0.2273	Bauß 2015
HM31	0.0750	Bauß 2015
HM32	0.0750	Bauß 2015

HM33	0.0750	Bauß 2015
C3C	0.0243	Bauß 2015
CAC	-0.1512	Bauß 2015
HV4	0.1500	Bauß 2015
CBC	-0.2199	Bauß 2015
HVC4	0.1000	Bauß 2015
HVT4	0.1000	Bauß 2015
C4C	-0.0463	Bauß 2015
CHD	-0.0079	Bauß 2015
HBM	0.1500	Bauß 2015
C1D	-0.0815	Bauß 2015
ND	-0.0709	Bauß 2015
C2D	0.1146	Bauß 2015
CMD	-0.2184	Bauß 2015
HM51	0.0750	Bauß 2015
HM52	0.0750	Bauß 2015
HM53	0.0750	Bauß 2015
C3D	0.0882	Bauß 2015
C4D	-0.0654	Bauß 2015
CHA	-0.0413	Bauß 2015
HGM	0.1500	Bauß 2015

CAD	-0.1851	Bauß 2015
HP61	0.1000	Bauß 2015
HP62	0.1000	Bauß 2015
CBD	-0.2979	Bauß 2015
HP63	0.1000	Bauß 2015
HP64	0.1000	Bauß 2015
CGD	0.3156	Bauß 2015
O1D	-0.4814	Bauß 2015
O2D	-0.4737	Bauß 2015

Reduced heme atom charges in multiples of the elementary charge.

atom	charge	source
FE	0.2500	Giammona 1984
NA	-0.1800	Giammona 1984
C1A	0.0300	Burggraf 2012
C2A	-0.0200	Burggraf 2012
CAA	-0.1600	Burggraf 2012
HP71	0.1000	Bauß 2015
HP72	0.1000	Bauß 2015
CBA	-0.3000	Burggraf 2012
HP73	0.1000	Bauß 2015
HP74	0.1000	Bauß 2015
CGA	0.3000	Burggraf 2012
O1A	-0.5000	Burggraf 2012
O2A	-0.5000	Burggraf 2012
C3A	0.0200	Burggraf 2012
CMA	-0.2650	Burggraf 2012
HM81	0.0750	Bauß 2015
HM82	0.0750	Bauß 2015
HM83	0.0750	Bauß 2015
C4A	0.0200	Burggraf 2012
CHB	-0.1100	Burggraf 2012

HDM	0.1500	Bauß 2015
C1B	0.0300	Burggraf 2012
NB	-0.1800	Giammona 1984
C2B	0.0200	Burggraf 2012
CMB	-0.2650	Burggraf 2012
HM11	0.0750	Bauß 2015
HM12	0.0750	Bauß 2015
HM13	0.0750	Bauß 2015
C3B	-0.0500	Burggraf 2012
CAB	-0.1300	Burggraf 2012
HV2	0.1500	Bauß 2015
CBB	-0.3300	Burggraf 2012
HVC2	0.1000	Bauß 2015
HVT2	0.1000	Bauß 2015
C4B	0.0200	Burggraf 2012
CHC	-0.1100	Burggraf 2012

HAM	0.1500	Bauß 2015
C1C	0.0300	Burggraf 2012
NC	-0.1800	Giammona 1984
C2C	0.0200	Burggraf 2012
CMC	-0.2650	Burggraf 2012
HM31	0.0750	Bauß 2015
HM32	0.0750	Bauß 2015
HM33	0.0750	Bauß 2015
C3C	-0.0500	Burggraf 2012
CAC	-0.1200	Burggraf 2012
HV4	0.1500	Bauß 2015
CBC	-0.3000	Burggraf 2012
HVC4	0.1000	Bauß 2015
HVT4	0.1000	Bauß 2015
C4C	0.0200	Burggraf 2012
CHD	-0.1100	Burggraf 2012
HBM	0.1500	Bauß 2015
C1D	0.0300	Burggraf 2012
ND	-0.1800	Giammona 1984
C2D	0.0200	Burggraf 2012
CMD	-0.2650	Burggraf 2012

HM51	0.0750	Bauß 2015
HM52	0.0750	Bauß 2015
HM53	0.0750	Bauß 2015
C3D	-0.0200	Burggraf 2012
C4D	0.0200	Burggraf 2012
CHA	-0.1100	Burggraf 2012
HGM	0.1500	Bauß 2015
CAD	-0.1600	Burggraf 2012
HP61	0.1000	Bauß 2015
HP62	0.1000	Bauß 2015
CBD	-0.3000	Burggraf 2012
HP63	0.1000	Bauß 2015
HP64	0.1000	Bauß 2015
CGD	0.3000	Burggraf 2012
O1D	-0.5000	Burggraf 2012
O2D	-0.5000	Burggraf 2012

Oxidized heme atomic radii in Å.

atom	radius	source
FE	0.69	Shannon 1976
NA	1.8240	Amber98, Tinker package
C1A	1.9080	Amber98, Tinker package
C2A	1.9080	Amber98, Tinker package
CAA	1.9080	Amber98, Tinker package
HP71	1.4870	H aliphatic, Amber98, Tinker package
HP72	1.4870	H aliphatic, Amber98, Tinker package
CBA	1.9080	Amber98, Tinker package
HP73	1.4870	H aliphatic, Amber98, Tinker package
HP74	1.4870	H aliphatic, Amber98, Tinker package
CGA	1.9080	Amber98, Tinker package
O1A	1.6612	Amber98, Tinker package
O2A	1.6612	Amber98, Tinker package
C3A	1.9080	Amber98, Tinker package
CMA	1.9080	Amber98, Tinker package
HM81	1.4870	H aliphatic, Amber98, Tinker package
HM82	1.4870	H aliphatic, Amber98, Tinker package
HM83	1.4870	H aliphatic, Amber98, Tinker package
C4A	1.9080	Amber98, Tinker package
CHB	1.9080	Amber98, Tinker package
HDM	1.4590	H on aromatic C, Amber98, Tinker package

C1B	1.9080	Amber98, Tinker package
NB	1.8240	Amber98, Tinker package
C2B	1.9080	Amber98, Tinker package
CMB	1.9080	Amber98, Tinker package
HM11	1.4870	H aliphatic, Amber98, Tinker package
HM12	1.4870	H aliphatic, Amber98, Tinker package
HM13	1.4870	H aliphatic, Amber98, Tinker package
C3B	1.9080	Amber98, Tinker package
CAB	1.9080	Amber98, Tinker package
HV2	1.4870	H aliphatic, Amber98, Tinker package
CBB	1.9080	Amber98, Tinker package
HVC2	1.4870	H aliphatic, Amber98, Tinker package
HVT2	1.4870	H aliphatic, Amber98, Tinker package
C4B	1.9080	Amber98, Tinker package
CHC	1.9080	Amber98, Tinker package
HAM	1.4590	H on aromatic C, Amber98, Tinker package
C1C	1.9080	Amber98, Tinker package
NC	1.8240	Amber98, Tinker package
C2C	1.9080	Amber98, Tinker package
CMC	1.9080	Amber98, Tinker package
HM31	1.4870	H aliphatic, Amber98, Tinker package

HM32	1.4870	H aliphatic, Amber98, Tinker package
HM33	1.4870	H aliphatic, Amber98, Tinker package
C3C	1.9080	Amber98, Tinker package
CAC	1.9080	Amber98, Tinker package
HV4	1.4870	H aliphatic, Amber98, Tinker package
CBC	1.9080	Amber98, Tinker package
HVC4	1.4870	H aliphatic, Amber98, Tinker package
HVT4	1.4870	H aliphatic, Amber98, Tinker package
C4C	1.9080	Amber98, Tinker package
CHD	1.9080	Amber98, Tinker package
HBM	1.4590	H on aromatic C, Amber98, Tinker package
C1D	1.9080	Amber98, Tinker package
ND	1.8240	Amber98, Tinker package
C2D	1.9080	Amber98, Tinker package
CMD	1.9080	Amber98, Tinker package
HM51	1.4870	H aliphatic, Amber98, Tinker package
HM52	1.4870	H aliphatic, Amber98, Tinker package
HM53	1.4870	H aliphatic, Amber98, Tinker package
C3D	1.9080	Amber98, Tinker package
C4D	1.9080	Amber98, Tinker package
CHA	1.9080	Amber98, Tinker package

HGM	1.4590	H on aromatic C, Amber98, Tinker package
CAD	1.9080	Amber98, Tinker package
HP61	1.4870	H aliphatic, Amber98, Tinker package
HP62	1.4870	H aliphatic, Amber98, Tinker package
CBD	1.9080	Amber98, Tinker package
HP63	1.4870	H aliphatic, Amber98, Tinker package
HP64	1.4870	H aliphatic, Amber98, Tinker package
CGD	1.9080	Amber98, Tinker package
O1D	1.6612	Amber98, Tinker package
O2D	1.6612	Amber98, Tinker package

Reduced heme atomic radii in Å.

atom	radius	source
FE	0.75	Shannon 1976
NA	1.8240	Amber98, Tinker package
C1A	1.9080	Amber98, Tinker package
C2A	1.9080	Amber98, Tinker package
CAA	1.9080	Amber98, Tinker package
HP71	1.4870	H aliphatic, Amber98, Tinker package
HP72	1.4870	H aliphatic, Amber98, Tinker package
CBA	1.9080	Amber98, Tinker package
HP73	1.4870	H aliphatic, Amber98, Tinker package
HP74	1.4870	H aliphatic, Amber98, Tinker package
CGA	1.9080	Amber98, Tinker package
O1A	1.6612	Amber98, Tinker package
O2A	1.6612	Amber98, Tinker package
C3A	1.9080	Amber98, Tinker package
CMA	1.9080	Amber98, Tinker package
HM81	1.4870	H aliphatic, Amber98, Tinker package
HM82	1.4870	H aliphatic, Amber98, Tinker package
HM83	1.4870	H aliphatic, Amber98, Tinker package
C4A	1.9080	Amber98, Tinker package
CHB	1.4590	H on aromatic C, Amber98, Tinker package

HDM	1.4590	H on aromatic C, Amber99, Tinker package
C1B	1.9080	Amber98, Tinker package
NB	1.8240	Amber98, Tinker package
C2B	1.9080	Amber98, Tinker package
CMB	1.9080	Amber98, Tinker package
HM11	1.4870	H aliphatic, Amber98, Tinker package
HM12	1.4870	H aliphatic, Amber98, Tinker package
HM13	1.4870	H aliphatic, Amber98, Tinker package
C3B	1.9080	Amber98, Tinker package
CAB	1.9080	Amber98, Tinker package
HV2	1.4870	H aliphatic, Amber98, Tinker package
CBB	1.9080	Amber98, Tinker package
HVC2	1.4870	H aliphatic, Amber98, Tinker package
HVT2	1.4870	H aliphatic, Amber98, Tinker package
C4B	1.9080	Amber98, Tinker package
CHC	1.4590	H on aromatic C, Amber98, Tinker package
HAM	1.4590	H on aromatic C, Amber99, Tinker package
C1C	1.9080	Amber98, Tinker package
NC	1.8240	Amber98, Tinker package
C2C	1.9080	Amber98, Tinker package
CMC	1.9080	Amber98, Tinker package

HM31	1.4870	H aliphatic, Amber98, Tinker package
HM32	1.4870	H aliphatic, Amber98, Tinker package
HM33	1.4870	H aliphatic, Amber98, Tinker package
HM33	1.4870	H aliphatic, Amber98, Tinker package
C3C	1.9080	Amber98, Tinker package
CAC	1.9080	Amber98, Tinker package
HV4	1.4870	H aliphatic, Amber98, Tinker package
CBC	1.9080	Amber98, Tinker package
HVC4	1.4870	H aliphatic, Amber98, Tinker package
HVT4	1.4870	H aliphatic, Amber98, Tinker package
C4C	1.9080	Amber98, Tinker package
CHD	1.4590	H on aromatic C, Amber98, Tinker package
HBM	1.4590	H on aromatic C, Amber99, Tinker package
C1D	1.9080	Amber98, Tinker package
ND	1.8240	Amber98, Tinker package
C2D	1.9080	Amber98, Tinker package
CMD	1.9080	Amber98, Tinker package
HM51	1.4870	H aliphatic, Amber98, Tinker package
HM52	1.4870	H aliphatic, Amber98, Tinker package
HM53	1.4870	H aliphatic, Amber98, Tinker package
C3D	1.9080	Amber98, Tinker package

C4D	1.9080	Amber98, Tinker package
CHA	1.4590	H on aromatic C, Amber98, Tinker package
HGM	1.4590	H on aromatic C, Amber99, Tinker package
CAD	1.9080	Amber98, Tinker package
HP61	1.4870	H aliphatic, Amber98, Tinker package
HP62	1.4870	H aliphatic, Amber98, Tinker package
CBD	1.9080	Amber98, Tinker package
HP63	1.4870	H aliphatic, Amber98, Tinker package
HP64	1.4870	H aliphatic, Amber98, Tinker package
CGD	1.9080	Amber98, Tinker package
O1D	1.6612	Amber98, Tinker package
O2D	1.6612	Amber98, Tinker package