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Large-scale virtual high-throughput screening for the identification of new battery electrolyte solvents: evaluation of electronic structure theory methods

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Abstract

The performance of semi-empirical quantum mechanical (SQM), density functional theory (DFT) and wave function theory (WFT) methods is evaluated for the purpose of screening a large number of molecular structures with respect to their electrochemical stability to identify new battery electrolyte solvents. Starting from 100000 database entries and based on more than 46000 DFT calculations, 83 candidate molecules are identified and then used for benchmarking lower-level computational models (SQM, DFT) with respect to higher-level WFT reference data. A combination of SQM and WFT methods is suggested as screening strategy at electronic structure theory level. Using a subset of over 11000 typical organic molecules and based on over 22000 high-level WFT calculations, several simple models are tested for the prediction of ionization potentials (IPs) and electron affinities (EAa). Reference data is made available for the development of more sophisticated QSPR models.

1. Introduction

Increasing global energy demand and rising carbon dioxide emission together with finite fossil fuel supplies and the expectation of soaring fuel prices have brought about the urgent need for renewable energy sources. Steadily harvesting large amounts of renewable energy poses a great scientific and technological challenge especially for industrialized countries. Even with sufficient amounts of renewable energy accessible, the need to store, distribute and efficiently utilize this energy presents us with daunting scientific and technological problems. Personal transportation is an area with major impact on the energy balance of western and developing countries and large-scale sustainable energy use in this sector will not be possible without substantial changes to current automobile technology.[1] The two most promising candidates to power future mobility concepts are fuel cells and advanced secondary batteries. Both technologies suffer from limitations that scientists strive to overcome within the next decades (like high costs for fuel cells and low energy densities for batteries) and can not be successful without advances beyond the area of science and technology (for instance concerning the infrastructure for charging and/or fueling). Very likely, both advanced batteries and fuel cells will play important roles for the electrification of the automobile.[1] As batteries will contribute substantially to future car making value chains, economical reasoning has become a major driving force for battery research. Current systems cost about 500 to 750 $ per kWh and can supply 150Wh per kg, improving this up to 250$ per kWh and 300Wh per kg within the next decade seems realistic and would be a major step forward for clean mobility concepts based on secondary batteries. It is important to keep in mind that the economic boundary conditions arise from a complex socio-economic process: Very important factors for the success of electric vehicles are carbon dioxide regulations and costumer sentiments (for instance the presumed loss of mobility or ’range anxiety’) which both might change drastically over comparably short time spans. The most pressing issue in reach of materials scientists is probably to improve the safety of battery devices, for instance by developing electrolyte solvents with higher thermal stability. The changes about to come are predicted to affect societies all around the world and accordingly several programs were initiated to speed up innovation in battery research.[2] This agenda is not believed to be futile, because basic research into electrochemistry still offers many opportunities so that future battery systems are predicted to be distinctively different from current technology, rendering previous knowledge less important. It will nevertheless require determined efforts to transform programmatic research infrastructure investments into actual scientific and technological successes. Beyond high voltage transition metal cathodes, carbon or silicon based nanocomposite anodes and polymer gel or ionic liquid electrolytes as well as optimized production processes, especially so called ’superbatteries’ (Lithium-Sulfur[3] or Lithium-Air[4]) are intensely investigated. Two areas with opportunities even for short-term scientific and technological impact are the development of better electrolytes and the systematic application of computational chemistry techniques. According to the great importance of cathode materials for the energy density of batteries, these and to a somewhat lesser extent anode materials have attracted more interest than electrolytes over the last decades, so that the latter are now more and more often found to be roadblocks for further improvements.[5–7] Similarly battery research has received substantial attention from theoreticians applying computational methods, but most often the focus lay again on electrode materials,[8,9] probably also fostered by the solid-state physics background of most of the scientists involved. As organic solvent molecules are important components of state-of-the-art electrolytes, it seems to be very likely that the search for better electrolytes can greatly profit also from the systematic application of molecular electronic structure theory approaches. This might be true not only for the optimal interfacing of electrodes and electrolytes in conventional systems but even for the development of electrolyte systems for superbattery chemistries, see for instance a series of very interesting studies from Bryantsev and co-workers at Liox Power on electrolyte components for Lithium-Air batteries.[10–12] Our goal is to develop a computational approach for the systematic and large-scale screening of electrolyte components. Here we present results for the first step in this program: the evaluation of computational models for the prediction of electrochemical stability window rankings. At this point we do not take solid-electrolyte-interface (SEI) formation into account, though we intend to do so in the future.

2. Theoretical considerations

Theory can contribute to battery research with insight and innovation: Concerning insight, theory can help to understand basic processes, concerning innovation, theory can help to set up knowledge-driven schemes for designing new materials or processes, thereby systematically transferring insight into innovation. Screening is concerned with the latter one, which means after knowing essential properties for specific problems, it tries to answer the question of how a thing looks like which does a better job at it. This again has two aspects, the findings of new candidates to test, but also the identification of emergent ’rules of the game’. (Like ’Does fluorination systematically lead to higher redox stability?’ or ’Is multifunctionalization advantageous?’ and so on.) When screening, the goal is to make best possible suggestions for what to do experiments on next. As the suggestions will almost always be based on simplified model systems and approximate computational methods, the results should be taken with the appropriate care, especially as sometimes seemingly simple questions require very high-level computational methods to be answered correctly.[13] Screening furthermore has to be guided by clearly defined objectives, in the case of battery electrolyte solvents this boils down to specific physical and chemical properties which are wanted or even necessary: The materials should remain stable and liquid under operation conditions, it should be doing well at solving salts and transporting ions and it should be as safe and cheap as possible. This results in a first list of properties to screen for, including a high (electro-)chemical stability (the electrochemical stability window), melting and boiling points in the right region, a high dielectric constant but a low viscosity, a high Li-ion conductivity $(> 10^{-4} S/cm)$ together with a low electronic conductivity $(< 10^{-10} S/cm)$, low (or no) flammability and disposition to explode, low toxicity and last but not least low costs. Almost all these properties can in principle be derived from computations, but especially the collective ones are very costly to get in terms of computation time. The above list is anyhow not yet complete, as we have so far not talked about chemical reactivity, which turns out to be the single most important factor at least for currently processed solvents, as their special feature is the formation of a solid-electrolyte-interface (SEI) layer, which keeps the majority of solvent molecules safe despite an insufficient electrochemical stability.[14,15]

Accordingly, recent theoretical work on electrolytes focused on this process: Apart from density function theory (DFT) studies on solvent decomposition processes,[16,17] also reactive force field molecular dynamics (MD) simulations[18,19] and even DFT MD simulations on the initial stages of SEI formation[20–22] were performed. Fewer studies investigated other properties at comparably high level.[23] Recent theoretical work on screening electrolytes includes a number of small-scale screening studies with promising results: Ceder and co-workers calculated the electrochemical windows of 6 ionic liquids at DFT level,[24] Han *et al.* investigated the electronic properties of 108 candidate molecules again with DFT,[25] Hall and Tasaki studied the electronic properties for 7000 ethylene carbonate (EC) derivatives with the about 1000 times faster semiempirical PM3 method,[26] Park *et al.* calculated electronic properties and Lithium binding affinities for 32 molecules with DFT[27] To not give a wrong impression, it should be mentioned, that overall theoretical work on batteries in the last years more often covered device properties or electrode materials: To name just a few examples, Sastry and co-workers used mesoscale modeling approaches to gain further understanding of conduction phenomena in batteries,[28] Kaxiras and co-workers investigated the deformation of silicon electrodes,[29] Ceder and co-workers looked into the thermodynamics and kinetics of Li/graphite intercalation[30] and developed a computational screening approach for cathode materials.[31–34]

Screening itself can be broken down into three tasks: The generation or retrieval of structures to screen, the evaluation according to specified parameters and the efficient analysis of the results, which plays an essential role as soon as large data sets are coming into play. Initially, structures can be taken from existing data bases with moderate effort. Later on, the more rewarding path will very likely be the knowledge-constrained randomized creation of electrolyte-specific structure data bases. Concerning the second task, structure evaluation, mostly calculated electrochemical stabilities were successfully used as parameter to screen for electrolyte components within in a small number of small-scale exploratory studies (with[26,27] as probably the most promising ones). Because of an increasing number of both test candidates and screening parameters, also the final task of analyzing the screening results will need to be based on sophisticated approaches. Fortunately, several approaches developed for virtual drug design within the field of chemoinformatics can readily be adapted for structure generation and analysis. To improve upon the current state of research, the two most important steps are: Firstly, the development of computational approaches for the efficient description of chemical reactivity related screening parameters, for instance to predict the SEI forming abilities of solvent molecules. Secondly, the coverage of more crucial physical properties, making use of the most efficient methods for each sub-task, including empirical approaches where necessary. While attempting to tackle these problems we saw the need to first take one step back again and evaluate the available computational methods for the description of the most basic property of interest: the electrochemical stability. DFT methods are sometimes taken to be the optimum approach for the calculation of material properties, but as we are concerned with small organic molecules, one should be aware that quantum chemistry actually has a lot more (and especially more accurate tools) to offer. Also when screening we are only interested in the correct ranking of candidates and do not worry about any shift between calculated and experimental values, so that we can be better off with a faster method as long as it allows us to correctly pick the top few hundred candidate molecules. The following is a first evaluation of the 'standard toolbox' of quantum chemistry for this purpose.

3. Computational Details

Semi-empirical AM1[35] and PM6[36] calculations were done with MOPAC2012,[37] making use of the MOZYME linear-scaling algorithm and the COSMO[38] solvation model. PBE[39] and and B3LYP[40,41] DFT, as well as Hartree-Fock (HF) and RI-MP2 calculations have been performed with TURBOMOLE 6.4,[42,43] using D2 dispersion corrections,[44] and the RI approximation for two-electron integrals.[45,46] LPNO-CEPA1[47] (CEPA in the following, see explanation below) calculations were done with ORCA 2.8.[48] TZVP and TZVPP AO basis sets[49] were employed for Turbomole and ORCA calculations. The accurate treatment of anions usually requires additional diffuse functions, which were taken from the Dunning aug-cc-pVTZ basis sets[50] to form what we call aTZVPP basis sets here. Simpler models are fitted using multi-linear regression within the R statistics package.

4. Benchmark set generation and screening results

We aim here at finding polar-aprotic, organic solvents with a higher electrochemical stability than ethylene carbonate (EC). For this purpose, 100000 molecules were gathered from public databases, about 25000 were selected as possible organic liquids by allowing no other than 1st and 2nd row elements and no more than 12 heavy atoms. If not mentioned otherwise, MMFF94 (force field) optimized geometries are used, see below for discussion of the impact of this approximation. About 23000 systems were aprotic and subjected to PBE/TZVP DFT calculations, in which 1200 molecules were found to have a HOMO/LUMO gap larger than EC, indicating a higher electrochemical stability. 200 of these had a dipole moment larger than 1 Debye, i.e. were polar. For this first benchmark study we furthermore excluded all systems with elements other than H, C, N, O, F, P, S, and required them to have at least 1 C atoms and more elements than just H, C, F, thereby focusing on usual organic molecules (though especially B and Si containing solvents clearly deserve our future attention). This way, we arrived at 83 molecules out of 100000 database entries, which were used for the systematic benchmarking of quantum chemical methods described below.

Among our 83 candidate molecules we have a rather large number of nitriles (with acetonitrile as one hit), some di-nitriles (with adiponitrile as one hit, recently suggested as new electrolyte solvent[51]), a tri-nitrile, and a collection of fluoro-ethers, poly-ethers, sulfones, sulfonamides, as well as some unusual cases. We see this as a very promising result, because we were able to correctly identify a number of compound classes from which molecules were suggested as new electrolyte solvents over the last decades,[52] already at this very early stage of our screening efforts. Our candidate molecules consist of 3 to 12 heavy atoms (6-33 atoms overall) and most of them contain only 1 or 2 'functional' (hetero-)atoms. The few cases with up to 6 hetero-atoms belong to the electrochemically most stable candidates, which supports recent claims that multifunctionalization is a promising way to better electrolyte solvents.[53] The collection of candidate molecules will be presented elsewhere after further research, here we would like to focus on the evaluation of computational methods.

To find out whether simpler empirical models could be an alternative to electronic structure theory methods for our purpose, further investigations were done using the full set of over 23000 aprotic molecules and a sub set of 11412 'typical organic' molecules: PM6 calculations for the full set and CEPA calculations for the organic set are compared to each other and used as reference data for the evaluation of empirical models based on the number of specific atoms, bonds, bond-types or functional groups in the respective molecules.

5. Evaluation results and discussion

The electrochemical stability window of a compound can be computed from its oxidation and reduction potentials (plus an additional shift for the chosen reference electrode):

$$V_{ox} = -\frac{\Delta G_{ox}}{nF} \qquad V_{red} = -\frac{\Delta G_{red}}{nF}$$

For this, one needs to calculate the Gibbs free energies of oxidation and reduction:

$$\Delta G_{ox} = \Delta G(X) - \Delta G(X^{+}) \qquad \Delta G_{red} = \Delta G(X^{-}) - \Delta G(X)$$

The individual free energies can be computed from electronic energies when zero-point and thermal enthalpic, entropic, as well as solvation effects are known:

$$\Delta G = \Delta H - T\Delta S = \Delta E + \Delta E_{ZVPE} + \Delta H_T - T\Delta S + \Delta G_{solvation}$$

Solvation effects can be taken into account rather easily and with acceptable accuracy via implicit solvent models (approximating the solvent environment as polarizable continuum),[38] but enthalpic and entropic contributions require rather costly frequency calculations. Most of the enthalpic, entropic and solvation effects can be assumed to cancel out to a large extent when computing the difference between neutral and charged states, so that the differences of electronic energies, i.e. the electron affinity (EA) and ioniziation potential (IP), can be used as an estimate for the oxidation and reduction potentials

$$\Delta G_{ox} \approx IP = \Delta E_{ox} = E(X) - E(X^{+}) \qquad \Delta G_{red} \approx EA = \Delta E_{red} = E(X^{-}) - E(X)$$

According to Koopman's theorem, EA and IP values can in turn be estimated from the energies of the lowest unoccupied (LUMO) and highest occupied molecular orbital (HOMO)

$$IP \approx -E_{HOMO} \qquad EA \approx -E_{LUMO}$$

This is another sizable reduction of computational efforts, as now only the neutral system needs to be processed, and accordingly most studies on electrochemical stability windows made use of this simplification.

We have calculated MO energies, ΔE and ΔG values with and without solvation effects for a number of different computational approaches, to systematically evaluate the impact of the different approximations and the performance of the different quantum chemical methods. The approaches which we have tested include the two semiempirical quantum mechanical (SQM) methods AM1 and PM6 (parametrized wave function theory methods, about three orders of magnitude faster than DFT, but often very close in accuracy[54]), DFT-methods at different theoretical level (the generalized gradient approximation (GGA) functional PBE and the hybrid B3LYP functional), Hartree-Fock, the MP2 perturbation theory approach, and a higher-level wave function theory method, the coupled electron pair approximation or CEPA (significantly slower than DFT for large systems, but also substantially more accurate for complicated cases[47]).

This choice of methods was based on an initial check with respect to experimental values: Recently, we have published an extensive comparison of the performance of SQM and DFT methods, using a large benchmark database.[54] Two subsets of this database, the G21EA and G21IP sets, were designed for the evaluation of computed electron affinities and ionization potentials in comparison to experimental data. In addition to the SQM and DFT data published before, we present here HF, MP2 and CEPA values for these benchmark sets in table 1. From this table it can be seen that all methods except PM6 perform better for IPs than for EAs. The best suited SQM methods are the OMx orthogonalization corrected models by Thiel and co-workers,[55] but these are parametrized for few elements only, which is why we had to resort to AM1 and PM6 for further tests. Turning to the DFT results, we find PBE best for EAs and PBE as well as BP86 and B3LYP best for IPs. PBE and BP86 are general gradient approximation (GGA) functionals, while B3LYP is a hybrid DFT functional, and we therefore chose PBE and B3LYP for the following tests. Among the WFT methods, the CEPA method stands out as most accurate even in comparison to DFT methods. Also EA values are very good, when diffuse functions are added to the basis set. This gives us the opportunity to evaluate the performance of lower-level (SQM and DFT) methods in comparison to the higher-level CEPA values even for cases where no experimental data is available. Based on the comparison to experimental values we accordingly continued with the above listed methods for the systematic tests on our collection of candidate molecules, now using theoretical reference values.

Tables 2 to 8 present the results for these tests in the form of correlation factors, i.e. measures for the correlation between two sets of datapoints. We use both Pearson R values, measuring linear correlation, and Kendall τ values, measuring non-linear or rank-correlation (the correlation between the actual ranking of values). Especially for the later case, a high correlation factors thus indicates, that the same ranking information is obtained, though the two data sets might be systematically shifted and/or scaled with respect to each other. For screening purposes, we are looking for the computationally cheapest method, that reproduces the ranking of our highest-level method with acceptable accuracy. Table 2 shows the effect of using the orbital approximation instead of calculating ΔE values. Table 3 illustrates which methods are best suited to reproduce our highest-level (LPNO-CEPA1/aTZVPP) results. Table 4 takes a closer look at the EA values of Table 2, showing correlation factors after adjusting the reference for possible errors due to problems with negative electron affinities (see below for details). Table 5 shows the effect of using a larger basis set for the DFT and WFT (i.e. HF, MP2, CEPA) methods. Table 6 illustrates the impact of solvation effects, included via the COSMO implicit solvent model. Table 7 presents a comparison between values calculated with geometries optimized at the respective level of theory with calculations based on force field (MMFF94) optimized geometries. Table 8 compares $\Delta E_{Red/Ox}$ and $\Delta G_{Red/Ox}$ values, the latter including zero-point and thermal enthalpic, as well as entropic effects.

A) Orbital approximation Perusing the EA values of table 2, we find correlation factors of about -0.6 to -0.7 for DFT and WFT methods with TZVPP basis sets, -0.5 and -0.8 for PBE and CEPA for the augmented aTZVPP basis set, and an almost perfect correlation for AM1 and PM6 (-0.97 for both). Turning to the IP values, we find correlation factors of about -0.4 to -0.8 for DFT and WFT methods with TZVPP basis sets, -0.7 and -0.5 for PBE and CEPA for the augmented aTZVPP basis set, and again an almost perfect correlation for AM1 and PM6 (-0.98 for both). This suggests, that first of all, the orbital approximation is quite bad for DFT and WFT, but (due to parametrization) excellent for semi-empirical methods. Our values here are worse than the better correlation values usually observed by for instance Dixon and co-workers,[56] because we look at the 'worst case scenario' of a comparably narrow window of EA and IP values from the 83 most stable compounds out of 100000. The changing correlation factors with increasing basis set for PBE and CEPA show that there is indeed (as expected) a significant effect on EA values from including diffuse basis functions (see also below). The lowering of the correlation factor with an increasing basis set for PBE indicates the lower quality of unoccupied orbitals in Kohn-Sham DFT, while the opposite trend for CEPA indicates the higher quality of orbitals for this correlated WFT method. The orbital approximation seems to work best for the B3LYP hybrid DFT method (with the exception of PM6 of course) and worst for MP2, but can overall be recommended only for semi-empirical quantum mechanical methods, not for DFT and WFT methods, as the advantage of the presumably higher accuracy of the latter ones is lost when applying this approximation.

B) Comparison of methods Comparing different methods in table 3, we find correlation factors for EA values of 0.4 to 0.5 for DFT and WFT methods apart from CEPA (for which we again see a pronounced basis set effect). For IP values, correlation factors for DFT/WFT methods are 0.5 up to 0.8 for MP2 (excluding again CEPA). Looking at AM1 and PM6, we find a very high correlation for IPs, but no correlation at all for EA values. This brings us to a not yet discussed problem with our EA reference values: Direct evaluation of electron affinities is unreliable when the affinity is negative, which indicates that the anion is unstable with respect to electron loss. In this case, a strong basis set dependency is observed and the affinity is becoming near zero as diffuse functions are added. With medium-sized basis sets reasonable estimates are obtained, because of an artificial binding of the electron by the finite basis set. A thorough discussion of the problem can be found by Tozer and De Proft, who also suggest using an approximation for the electron affinity which avoids these problems:[57,58]

$$EA = -(E_{LUMO} + E_{HOMO}) - IP$$

To analyze this further, we have tested their suggestion on our data. We find big differences between calculated EAs and EAs estimated according to Tozer and De Proft which indicates, that our EA reference data – as well as all other WFT and DFT values – do indeed suffer from the problem. Using the corrected values (see table 4), we find a good correlation between the CEPA values with different basis sets, and an acceptable correlation for MP2 and SQM values in comparison to our corrected reference. Interestingly, the correlation for all DFT methods is negative, probably because molecular orbital energies are underestimated even more than IP values at this level, which leads to a growing divergence with higher electron affinities. A more definite statement is unfortunately not possible on the basis of our data, because the overall range of EA values at CEPA/aTZVPP level is only 2 eV, and the average deviations of the DFT values are of the same size. To summarize: The computation of accurate (negative) EA values is challenging for all lower-level quantum chemical methods, EAs can be estimated from orbital energies and IP values, SQM and WFT methods seem to have an advantage here.

C) Other effects Table 5 shows that the TZVPP basis set is (as expected) good enough for the calculation of IPs (neutral and positively charges species), but no so for EAs (involving negatively charges species). The augmentation has a bigger impact on the correlated WFT method (again as expected), but the difference is also significant for the DFT method, though probably acceptable for ranking purposes. Computations with the augmented basis set take about 10 times longer, which would increases the cost of high-throughput screening for reduction potentials based on the calculation of ΔE values with basis set dependent methods by a significant amount. Table 6 illustrates, that solvent effects have a comparably small – though for HF and MP2 still sizable – impact on the rankings. Table 7 shows the difference between calculations on force field (MMFF94) and quantum mechanically optimized geometries, which is reasonably small only for IPs, but quite substantial for EA values. The high correlation value of PBE for IPs, together with the low corresponding value for PM6, indicate a rather good quality of the force field structures, which seems to be getting worse under optimization at SQM-level. Enthalpic and entropic effects can on the other hand be neglected as shown in table 8, as they seem to cancel out almost perfectly when calculating ΔE values.

To summarize our findings:

- using the orbital approximation can not be recommended for DFT and WFT methods
- we find no substantial benefit from DFT over SQM methods for the calculation of ionization/oxidation potentials for ranking purposes
- electron affinities/reduction potentials are on the other hand a problem for SQM methods, but DFT and WFT methods are plagued with their own problems related to negative electron affinities, so that again no real benefit from DFT over SQM methods is found for ranking purposes
- solvation and especially geometry optimization have impact on the ranking at least for electron affinities, the latter effect seems to be treated with lower accuracy at SQM than at DFT level
- enthalpic and entropic contributions can be neglected for ranking purposes

This leads us to the following recommendations:

- one should either use SQM methods and the orbital approximation or DFT/WFT methods and ΔE values (the additional effort of calculating ΔE values is wasted for SQM methods, the computing time saved with the orbital approximation is not worth the loss of accuracy for DFT/WFT methods)
- therefore, initial screening should be done with SQM methods and the orbital approximation, while later stage screening should be done with DFT/WFT methods and ΔE values

- geometry optimization and solvent effects should be taken into account at this later stage (they are important especially for electron affinities, but of lower quality when calculated at the SQM level)
- we suggest to extrapolate electron affinities from molecular orbital energies according to Tozer $et\ al.$ to avoid problems with negative electron affinities and remove the need for calculations on negatively charges species (which in turn alleviates the need for geometry optimization and solvent modeling)
- we suggest the higher-level WFT approach LPNO-CEPA/1 as a more accurate alternative to DFT for small organic molecules, for which the additional computational cost is negligible

Further investigations were done on the full set of over 23000 aprotic molecules and a sub set of 11412 typical organic molecules with the aim of testing simpler models for the prediction of IP and EA values. Tables 9 and 10 present the results for these tests: Table 9 lists R and τ values for the comparison of PM6 and CEPA calculations on the organic set. We again find that the orbital approximation works almost perfectly for SQM and quite badly for WFT methods. Correlation is good between PM6 and CEPA IP, but not for EA (though acceptable for LUMO) data, with R values of 0.89 and 0.31. Table 10 presents correlation factors for IP and EA estimates from simpler models. If only based on information about the number and type of atoms, R values of about 0.3 are found. With information about the number of bonds between specific atom pairs, R values are improved to about 0.6. Using PM6 reference data and only the organic set, our best model gives R values of 0.81 for IPs and 0.88 for EAs. Mean absolute deviations (MADs) are 0.38 eV and 0.40 eV for the IP values between 6 and 14 eV and the EA values between -4 and 6 eV, thus giving average errors below 5 %. Comparing CEPA and PM6 values we found a bimodal distribution of PM6 numbers with respect to the CEPA data; PM6 seems to systematically underestimate EA values for more delocalized structures. Because of this observation we switched to CEPA reference values for fitting our final model, for which we get R values of 0.79 and 0.64 for IPs and EAs. This is in agreement with the systematically wrong description of EAs based on structural features, to which the simple structure-based model can more easily be fittted. We finally also tested models based on information about the number and type of functional groups, but found no large improvements from this treatment. Comparison of the data in table 9 and 10 shows that using our final model can be advantageous over applying SQM methods especially for EA values. We would nevertheless like to encourage the development of more sophisticated QSPR model for IP and EA values with supplying our CEPA reference data as Supporting Information.

6. Conclusions

We have presented a first large-scale virtual high-throughput screening test with DFT calculations on more than 23000 small molecules, which allowed us to correctly identify a number of compound classes from which molecules were suggested as new electrolyte solvents over the last decades.[52,59,60] In addition, some new solvent and/or additive candidate structures were identified and will be subject to further research now. The main goal of our study was the evaluation of computational models for the screening of advanced battery electrolyte solvents with respect to electrochemical stability. Based on the comparison with higher-level wave function theory reference values, we suggest to use semi-empirical quantum mechanical methods and the orbital approximation at the initial screening stage, and rescore the top results with the higher-level wave function theory LPNO-CEPA/1 method by calculating ΔE values on optimized geometries and including solvent effects. Finally, a simple model for the prediction of IP and EA values for typical organic molecules is presented with a performance similar to SQM methods, and high-level WFT reference data for over 11000 typical organic molecules is supplied for the development of more sophisticated QSPR models by other groups.

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Supporting information

Structures and CEPA reference values for the organic CEPA data set.

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Table 1: Mean deviations (MDs) and mean absolute deviations (MADs) in kcal/mol for the G21IP and G21EA benchmark sets.

	EA	IP
SQM methods		
OM1[a]	24.45	20.64
AM1[a]	23.03	20.32
PM6[a]	22.06	37.99
OM2[a]	11.70	10.76
OM3[a]	9.91	10.61
DFT methods		
TPSS/TZVP[a]	10.58	5.40
BLYP/TZVP[a]	9.52	5.36
B3LYP/TZVP[a]	9.47	4.84
BP86/TZVP[a]	7.49	4.81
PBE/TZVP[a]	7.00	4.64
WFT methods		
HF/TZVP	37.16	24.00
MP2/TZVP	16.54	6.74
CEPA/TZVPP	13.79	3.59
CEPA/aTZVPP	3.61	2.64

[a] data from reference[54]

Table 2: Pearson R / Kendall τ values for the correlation between $\Delta E_{Red/Ox}$ data and HOMO/LUMO energies

	EA vs LUMO	IP vs HOMO
PBE/TZVPP	-0.67/-0.50	-0.66/-0.51
PBE/aTZVPP	-0.49/-0.45	-0.68/-0.52
B3LYP/TZVPP	-0.67/-0.54	-0.79/-0.63
HF/TZVPP	-0.61/-0.52	-0.56/-0.41
MP2/TZVPP	-0.59/-0.48	-0.44/-0.28
CEPA1/TZVPP	-0.67/-0.63	-0.55/-0.34
CEPA1/aTZVPP	-0.81/-0.70	-0.53/-0.35
PM6	-0.97/-0.85	-0.98/-0.89
AM1	-0.97/-0.85	-0.98/-0.89

Table 3: Pearson R / Kendall τ values for the correlation between $\Delta E_{Red/Ox}$ data and LPNO-CEPA/aTZVPP reference values

	EA	IP
PBE/TZVPP	0.52/0.42	0.53/0.38
PBE/aTZVPP	0.42/0.42	0.51/0.35
B3LYP/TZVPP	0.50/0.41	0.58/0.41
HF/TZVPP	0.46/0.32	0.60/0.41
MP2/TZVPP	0.47/0.33	0.76/0.58
CEPA/TZVPP	0.74/0.61	0.97/0.88
PM6	0.04/-0.02	0.80/0.62
AM1	0.04/-0.02	0.80/0.62

Table 4: Pearson R / Kendall τ values for the correlation between $\Delta E_{Red/Ox}$ data and corrected (see text for details) LPNO-CEPA/aTZVPP reference values

	EA
CEPA/TZVPP	0.77/0.57
MP2/TZVPP	0.52/0.36
B3LYP/TZVPP	-0.59/-0.47
PBE/aTZVPP	-0.61/-0.49
PBE/TZVPP	-0.66/0-0.49
HF/TZVPP	0.16/0.11
PM6	0.45/0.29
AM1	0.45/0.29

Table 5: Pearson R / Kendall τ values for the correlation between $\Delta E_{Red/Ox}$ data calculated using aTZVPP and TZVPP basis sets

	EA	IP
PBE	0.91/0.69	1.00/0.99
CEPA	0.74/0.61	0.97/0.88

Table 6: Pearson R / Kendall τ values for the correlation between $\Delta E_{Red/Ox}$ data calculated with and without COSMO solvation

	EA	IP
PBE/TZVPP	0.94/0.72	0.97/0.80
B3LYP/TZVPP	0.91/0.60	0.95/0.77
HF/TZVPP	0.83/0.56	0.80/0.62
MP2/TZVPP	0.83/0.55	0.76/0.55
PM6	0.92/0.74	0.95/0.80

Table 7: Pearson R / Kendall τ values for the correlation between $\Delta E_{Red/Ox}$ data using optimized and MMFF94 geometries

	EA	IP
PBE/TZVPP	0.71/0.40	0.97/0.85
PM6	0.83/0.73	0.71/0.51

Table 8: Pearson R / Kendall τ values for the correlation between $\Delta G_{Red/Ox}$ (excluding solvation effects) and $\Delta E_{Red/Ox}$ data

	ΔG_{Red} vs EA	ΔG_{Ox} vs IP
PBE/TZVPP	1.00/0.95	1.00/0.96
PM6	1.00/1.00	1.00/1.00

Table 9: Pearson R and Kendall τ values for the large set of 11412 organic molecules

	R	τ
PM6		
IP vs HOMO	-0.98	-0.90
EA vs LUMO	-0.99	-0.91
CEPA		
IP vs HOMO	-0.84	-0.67
EA vs LUMO	-0.58	-0.29
PM6 vs CEPA		
HOMO	0.86	0.68
LUMO	0.73	0.60
IP	0.89	0.74
EA	0.31	0.19

Table 10: Pearson R values for selected empirical models, Kendall τ values for the final model in parenthesis.

	IP	EA
atom based models		
no. of specific atoms	0.35	0.35
bond based models - ’full’ PM6 data set		
no. of HC bonds	0.30	0.47
no. of HN bonds	0.46	0.07
HC,HN	0.60	-
HC,HN,CN,CO,CS	0.63	-
HC,CC	-	0.51
HC,CC,CN,CS,CO	-	0.58
HC,HN,CC,CN,CO,CS,NO	-	0.62
18 types	0.65	0.65
18 types w/o outliers	0.67	0.71
bond based models - ’organic’ PM6 data set		
xx types	0.81	0.88
bond based models - ’organic’ CEPA data set		
xx types	0.79(0.59)	0.64(0.43)
functional group based models - ’organic’ CEPA data set		
xx types	0.81	0.66