

# Rapid flipping between electrolyte and metallic states in ammonia solutions of alkali metals

Corresponding Author: Professor Pavel Jungwirth

**This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.**

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The manuscript "Rapid flipping between electrolyte and metallic states in ammonia solutions of alkali metals" by Vitek et al. reports theoretical study of electrolyte-to-metal transitions (EMT) in lithium solution in liquid ammonia at various metal concentration by means of DFT-based molecular dynamics (MD), supplemented by GW band-structure calculations at selected configurations. In addition, the authors draw support of their results by analyzing previously published photoelectron (PE)spectra. They characterize the two distinct states of the system - electrolyte and metal-like - and reveal fast oscillations between the two. This dynamic equilibrium is supposed to explain the experimental spectroscopic evidence for the coexistence of the two systems: with and without band gap.

I believe that the topic is of interest for a wide range of natural scientists due to practical importance of ammoniated electrons and their fundamental value (the "blue solutions" are a part of a standard general chemistry curriculum and are well known to practically every chemist). The study is elegantly designed, consistently executed and well written. However, the methodology is compromised due to seemingly small flaws, which are known to have dramatic effects on the quality of the results. Those include the choice of density functional with little amount of exact exchange and the use of the improper MD sampling technique (thermostat) to evaluate dynamic properties of the system. Experimental validation could in principle lift the doubts, but it does not provide any insights into the dynamic properties in question, whereas the agreement with theory is at most mediocre (see, in particular, Fig. 5, panel b). I will elaborate on both point below.

Therefore, keeping in mind the boost a publication in the Nature family enjoys, I can't recommend publication of this work in Nature Communications due to questionable data quality. I strongly believe that neither the importance of the problem, nor the quality of images and text should not justify sloppy methodology and seemingly insufficient understanding of the underlying simulation methods.

I would, nevertheless, consider reviewing a revision if the work is appended with some more proper calculations to validate the current approach. Those should be based on a different functional and thermostat.

Major methodological issues:

1) It is known since at least 2005 that density functionals with increased amount of exact exchange are more suitable for simulating solvated electrons. Those come independently from Herbert/Head-Gordon, Turi, Pasquarello, Lan/Rybkin to name a few. All these groups are unrelated and base their conclusions on different criteria (binding energies, dynamics, band structures, spin-densities as compared to wave functions etc.) Although GW is relatively independent of the DFT reference, it can't correct the trajectory propagated by PBE0 (with only 25% of exact exchange). In the case where (I cite the authors) "properties depend very sensitively on minor changes in molecular geometry and electron density" the choice of functional is critical, but here it is selected uncritically and against a well established consensus.

2) The authors (in the SI) allege to have used the Nose thermostat for production runs, actually referencing Nose and Hoover, but not the Nose-Hoover (NH) chain (or was in the chain?), this observation itself being telling. Deriving dynamic properties (such as the frequency of oscillation between the metallic and electrolyte states) is a typical and sad error. The NH and many other thermostats based on aggressive velocity rescaling dramatically distort particle dynamics and generally inapplicable for properties such as diffusion, vibrations and indeed fast state oscillations. A converged (sic!) NH trajectory can give us an equilibrium constant between the electrolyte and metallic states (in terms of time distributions). The

information on their instant lifetimes and molecular mechanisms of transition are spurious. More to this, integrating several 1ps trajectories are a good strategy for probing dynamic properties with proper integrator (why not simply NVE or stochastic velocity rescaling?), but for the NH they are very far from convergence. That said, I believe that short-time fluctuations (main discovery of the work!) are very plausible, but I don't have to believe, it's science.

3) Experimental validation. The PE spectra (albeit with some assumptions) document the simultaneous presence of the species with and without band gap. However, they don't provide any insights in the dynamics properties (e.g. the oscillation time between the states). Although the presented picture explains the observation in general, no direct experimental support for is shown. Keeping in mind a very moderate agreement of the computed and experimental numbers, one shouldn't rule out the possibility that a different model reaches a better agreement.

## Reviewer #2

### (Remarks to the Author)

The manuscript by Jungwirth and co-workers presents an interesting perspective on solvated electrons in ammonia solutions. This work is a detailed continuation of their previous study on the gradual, non-first-order electrolyte-to-metal transition [Science 368, 1086-1091 (2020)]. Additionally, they found a rapid flipping between electrolyte and metallic states.

They have combined state-of-the-art hybrid functional-based molecular dynamics to obtain accurate dynamics and the GW method to accurately capture the electronic density of states of the solvated electron at various concentrations. The calculated density of states is further compared with experimental photoelectron spectroscopy. Overall, the manuscript is well-written, and the conclusion that both simulations and experiments evidence rapid flipping between electrolyte and metallic states is well-supported.

There are a few scientific issues that the authors need to address:

Regarding the calculations of DoS, are they all performed using GW methods? For instance, did the authors perform GW calculations for Figure 2 a, b? If the DoS are presented at different levels of theory, the authors should indicate the electronic structure theory used to obtain the DoS in the captions.

There is a follow-up question regarding the DoS, if Figure 2 is carried out using revPBE0 hybrid functional. In Section 4. Extended results in SI show the correlation between revPBE0 energies and the GW method for both orbital energy and band gap. revPBE0 with 0.25 HFX doesn't rule out the self-interaction error. This is evident as revPBE0 overestimates the HOMO and underestimates the LUMO, resulting in a smaller band gap compared to the GW method. One needs to use a hybrid functional with a higher fraction of HFX, such as about 40% HFX for water, which should fulfill the piecewise linearity of the functional upon fractional electron occupation [Phys. Rev. Research 3, 023182]. For its application to aqueous electrons, see [J. Phys. Chem. Lett. 2017, 8, 9, 2055–205] and [Angew. Chem. Int. Ed. 2022, 61, e202209398]. If one extrapolates the correlations between revPBE0 and GW band gap (Figure 4 a in SI), we can see that when the revPBE0 gap decays to 0, the GW still predicts a band gap of around 0.3 eV. Although the picture of flipping between electrolyte and metal might not change, the analysis of the 3.0 MPM would be less accurate. It may likely be only electrolyte, or at least less metallic.

## Reviewer #3

### (Remarks to the Author)

The authors present a computational study of lithium ammonia solutions across a concentration range of the electrolyte-to-metal transition in the corresponding solutions. They use ab initio molecular dynamics simulations based on a DFT approach to describe the dynamics of the system and calculate the density of states at selected snapshots. Furthermore, they calculate a spherical band structure to address the dispersion relation of electrons in these disordered liquid systems, and to better describe the band gap of these systems. For the latter task they use a specially developed computational tool. To verify their computational results, they compare their results to experimental photoelectron data obtained from previously published but re-evaluated liquid jet measurements.

They find, that with increasing metal concentration, the band gap of the system closes and fills, in agreement with a gradual electrolyte-to-metal transition. Most remarkably, they observe ultrafast flipping of the system between electrolytic and metallic behaviour on timescales of ~40 fs in the intermediate concentration regime, over which the gradual transition to the metallic phase occurs. This flipping behaviour, is attributed to minor changes in the molecular structural arrangement of the liquid, that can drastically change the electronic structure. They relate the observed temporal fluctuations of the electronic structure to previously observed spatial inhomogeneities and concentration fluctuations in alkali ammonia solutions of intermediate concentration.

I believe such studies are important in providing a deeper molecular level understanding of the fascinating behaviour of alkali ammonia solutions and their transition to a liquid metallic phase. Experimental studies alone, usually are not able to deliver such detailed molecular level insights. I believe the study is sound the results are novel and in principle well suited for publication in nature communications.

However, there remain a few open questions regarding the connection of the observed flipping between states and the transition to the metallic state as well as regarding the comparison between experimental data and computational results that, in my opinion, need to be addressed prior to publication.

1. While the finding of fluctuations between electrolytic and metallic states is fascinating, it does not become absolutely clear to me how this behaviour relates or contributes to the transition of the metallic phase. Can these fluctuations of the band structure with time really directly be connected to the spatial inhomogeneities and concentration fluctuations described in the introduction (bottom half of second column, page 1)? After all, the simulations in a small cell of 15 Å, with a fixed number of ammonia molecules and lithium atoms can not show fluctuations of the concentration? It could be helpful to more clearly explain the connection between these observations and the observed temporal fluctuations.

2. For the gradual transition to the metallic phase, it would be very interesting to see a direct comparison of the situation at various intermediate concentrations. While this is provided in figure 1 for some quantities it seems to be missing for some others.

- For example, the change of the spatial extent of the dielectrons (radius of gyration and Wannier orbitals) changes drastically between 3 and 6 MPM, with a much-decreased difference between metallic and electrolytic configurations at 6 MPM. Are these effects understood?
- the charge carrier mobility seems to significantly decrease for the metallic states of 6 MPM vs those at 3 MPM. Is this effect understood?
- For a gradual transition to the metallic phase I would have expected that at 6 MPM the system spends more time in metallic states than in the 3 MPM case, but this seems not to be the case. Do the authors understand why? I think these effects could and should be mentioned and possibly explained in the main text.

3. A brief comment on how the 100 frames for the band structures in figure 1 are selected would be helpful. Do these band structures only contain metallic frames or also electrolytic frames?

4. The method to separate the non-metallic photoelectron signals from the metallic ones for the 3.4 MPM photoelectron spectrum has not been reported in the prior publication (reference 5 in the main text), so this should be explained here. I assume it is based on the fitting procedure, which allows subtraction of the plasmon signals and subsequent creation of a type of masking filter to separate the strongly overlapping photoelectron bands corresponding to the metallic and electrolytic solvated electrons (figure 4 of reference 5), is this correct?

5. I find the comparison of the computational results to the experimental data not fully convincing:

- I find that the representation of the experimental signals without vertical axis scale is misleading. In reference 5 of the main text (i.e. the initial publication of the experimental work) it looks like the experimental signals for the electrolytic and metallic states are of very similar intensity, yet in figure 5 they are scaled very differently (panels b and c), as if the metallic photoelectron signal would only correspond to the very low calculated density of states close to the Fermi level. If this is the case, the largely different relative magnitudes may indicate a significant disagreement between the calculations and the experimental data, that would need to be addressed.
- Also in the conclusion they refer to this point again: "Moreover, we demonstrate that the densities of states of metallic configurations still to a large extent possess features pertinent to electrolyte configurations, with only a weak filling of the band gap." In my opinion this contradicts the experimental data in reference 5, which shows photoelectron signals rising toward Fermi level and a sharp band edge.
- Interestingly the calculated density of states for the metallic configurations in the 3 MPM case (panel a), shows also a bimodal structure in the lower energy peak (not visible in panel b due to the scaling). However, the authors do neither address this in the text, nor compare it to the experimental data.

Minor comments:

- It would be helpful to refer the reader to explicit sections in the SI, rather than referring the reader to the SI as a whole. It always took me some time to find the information relevant at a specific point of the main text.
- In the supplementary information, in the comparison of the ammonia 3a<sub>1</sub> density of states to the photoelectron data (figure 11) it does not become clear to me which features the authors think agree and which disagree. Do they assume all the fine structure is real? In reference 5 of the main text (i.e. the original publication of the experimental data) the changes to the 3a<sub>1</sub> band are described as a broadening and shift towards lower binding energy. In the representation in figure 11 I cannot clearly see this effect, or at least cannot judge if the calculations reproduce this effect.
- There exists a significant number of studies of solvated electrons in alkali-doped clusters of ammonia and other solvents, also covering a wide concentration range (not cited in the current manuscript). In the past it has been questioned if such studies can show bulk like electronic structure features, due to their limited system size. The system calculated here (64 ammonia molecules with up to 10 Li atoms) is comparable to the cluster systems studied experimentally. Is it clear that in the calculation the system size is big enough to predict bulk properties? If so, is there a clear argument that this is the case?
- Since the flipping between the electrolytic and metallic states is driven by minor changes to the molecular arrangement, the temperature of the sample should have an effect on the frequency of the flips. A full analysis of this temperature dependency is likely beyond the scope of this work, but it would be worth to state the simulated temperature of the system at some point in the main text.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In the revised version of the manuscript "Rapid flipping between electrolyte and metallic states in ammonia solutions of alkali metals" by M. Vitek et al., the most serious methodological issues have been addressed properly: the MD simulations have been redone in a proper ensemble with a suitable DFT functional with an increased amount of exact exchange. They present a methodologically interesting analysis of the functional effect on the results in the SI. I recommend to publish this version of the manuscript as is.

Reviewer #2

(Remarks to the Author)

The authors have addressed all the concerns raised. I recommend the manuscript for publication in its current form.

Reviewer #3

(Remarks to the Author)

As expressed in my previous comments, I believe the presented computational study reveals new insights into the molecular level properties of alkali solutions in liquid ammonia, specifically into the mechanisms driving the electrolyte to metal transitions at high alkali concentrations. I believe this study is in principle well suited for publication in Nature Communications. The authors have addressed most of my questions and concerns. There is in fact only one point that I think the authors did not address adequately, which is related to the comparison between their calculated DoS and the previous experimental results from liquid jet photoelectron spectroscopy (figure 5 in the main text).

I do not agree with the authors in their overall assessment, that "The general agreement between the computational and experimental time-averaged results thus demonstrates the effectiveness of the employed computational methodology, while also providing detailed insights into the electronic structure changes occurring during the EMT."

The only agreement I can see in figure 5 b and c is that the DoS of the metallic frames and the signal corresponding to conduction band electrons is non-zero at the Fermi level, while the DoS of the electrolyte frames and the experimental signal corresponding to solvated dielectrons is not. Given the previous sections of the manuscript, and the analysis of the experimental data, this would however be a rather trivial statement. The overall shape of the DoS is however completely different. In addition, the position of the DoS feature corresponding to the solvated dielectrons agrees with their experimental counterpart.

Claiming agreement in the Fermi edge region in figure 5 c, after rescaling the calculated metallic frame DoS (by what I estimate to be more than one order of magnitude) seems misleading to me. Claiming agreement in panel 5 b, between the electrolytic DoS and the experimental dielectron signal is possible, but the agreement with the metallic frame DoS or total (averaged over all frames) DoS would likely be similar.

I think there is a strong discrepancy between the calculations and the experimental data concerning the very low DoS at the Fermi level for the metallic frames, while the experimental data indicates equal intensity for conduction band electrons and solvated dielectrons. The authors comment on the fact that the DoS for metallic frames still shows a strong contribution of localized solvated dielectrons, making the comparison to the decomposed experimental data challenging. This seems to be a valid and interesting conclusion, but still the observed density of localized solvated dielectrons and delocalized conduction band electrons seems to disagree between experiment and calculation. A similar observation can be made in figure 5 d for the high alkali concentrations: At the Fermi level, the calculated DoS is much lower than indicated by the photoelectron signals. This disagreement for me seems to be the most important (and interesting?) observation from the comparison in figure 5.

In their reply to my previous comment regarding this, they give possible explanations for these discrepancies:

1. Possible differences in the photoionization cross sections and photoelectron angular distributions of conduction band electrons and solvated dielectrons
2. Possible differences in the surface activities of the different electronic species.

While this does not immediately seem very likely to me, the authors should discuss these possibilities in the main text, if they believe these points can explain parts of the observed discrepancies. Is there other possible (experimental or computational) explanations for the discrepancies?

Would it not be better to compare the calculated DoS averaged over all frames with the complete experimental photoelectron spectrum? Decomposing the photoelectron spectrum into localized and delocalized electrons seems unnecessary given the fact that also the metallic frames show still a substantial content of localized solvated dielectrons.

At the moment the comparison offered in figure 5, with the claim of agreement rather than discussion of possible origins of the discrepancies between calculations and previously reported experiments in my opinion weakens this overall strong manuscript considerably, and I believe this part should be improved prior to publication.

Version 2:

Reviewer comments:

### Reviewer #3

#### (Remarks to the Author)

I think the changes the authors made are moving in the right direction, but they have only addressed a part of the concerns I have formulated. They did barely change the discussion of the case of 3.0/3.4MPM. My apologies if these concerns were not formulated clearly enough before:

The comparison between experimental data and calculation for the intermediate concentration range seems dishonest to me. I understand that the binary decomposition of the experimental data is the only way to separate “metallic signals” from “electrolytic signals”. Experimentally these signals at 3.4 MPM concentration are roughly equal in intensity (as is clearly seen in the corresponding plots in the SI). The calculation at a similar concentration shows roughly ten times the DoS at binding energies corresponding to solvated (di)electrons than at binding energies corresponding to metallic conduction band electrons (as can be seen from the various lines in figure 5 c).

I cannot understand how this is only an “apparent” discrepancy. The picture given by the calculations is maybe more nuanced, but certainly is different.

The separation of “metallic” and “electrolytic” experimental electron signals for me seems to hide the fact that the two have (experimentally) the same intensities. Of course, the experiment cannot separate metallic frames from electrolytic frames, making the comparison imperfect. But the computational results can easily provide the information corresponding to the experimental results: What is the DoS at binding energies corresponding to solvated (di)electrons and what is the DoS corresponding to conduction band electrons close to the Fermi edge. This would correspond to the comparison of the sum of experimental signals of metallic and electrolytic electrons (total electron signal minus the plasmon signals) to the calculated density of states (total or only metallic frames), similar to the comparison the authors show in figure 5a for the purely metallic case.

In other words: The separation of the experimental signal into “electrolytic” and “metallic” electrons, does not make any sense for me. Instead their sum should be compared to the calculated DoS, and the discrepancies explained (photoionization cross sections? Surface activity of different electronic species etc?).

I think this comparison should be given in figure 5 and discussed.

As this comparison is not the main finding of this manuscript, I do not believe that there needs to be perfect agreement between calculations and experiments, but the comparison needs to be fair.

Version 3:

Reviewer comments:

### Reviewer #3

#### (Remarks to the Author)

I appreciate the changes made by the authors, with the direct and unambiguous comparison between the calculated density of states and the experimental photoelectron spectrum and the open discussion of possible reasons for the remaining observed discrepancies. With these modification, all my concerns are addressed adequately and I can fully recommend the publication of this manuscript in nature communications.

#### Minor comment:

The second sentence on page 6 seems to need correction.

**Open Access** This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

# Reply to reviews for: Rapid flipping between electrolyte and metallic states in ammonia solutions of alkali metals

December 13, 2024

**Dear editors,**

thank you for considering our manuscript “Rapid flipping between electrolyte and metallic states in ammonia solutions of alkali metals” for publication in the Nature Communications (Nat. Com.). We start by stating that we thank all the reviewers for their fair and positive assessment of our work and the constructive comments throughout. In particular, their suggestions to use hybrid functionals with a larger content of exact exchange led us to extensive recalculations. The new and more accurate results presented in the revised manuscript improve the fidelity of our computational predictions without changing qualitatively the original message. Also, we stress that the new calculations benchmark quantitatively against the GW method as now detailed in the SI.

The following comments and suggestions (in black) were raised by the reviewers. We thank the reviewers for their careful evaluation of our manuscript and appreciate their suggestions to improve the manuscript. Our point-by-point response to each issue is shown in [blue](#):

## Reviewer 1

### Comments

*The manuscript ” Rapid flipping between electrolyte and metallic states in ammonia solutions of alkali metals” by Vitek et al. reports theoretical study of electrolyte-to-metal transitions (EMT) in lithium solution in liquid ammonia at various metal concentration by means of DFT-based molecular dynamics (MD), supplemented by GW band-structure calculations at selected configurations. In addition, the authors draw support of their results by analyzing previously published photoelectron (PE)spectra. They characterize the two distinct states of the system - electrolyte and metal-like - and reveal fast oscillations between the two. This dynamic equilibrium is supposed to explain the experimental spectroscopic evidence for the coexistence of the two systems: with and without band gap.*

*I believe that the topic is of interest for a wide range of natural scientists due to practical importance of ammoniated electrons and their fundamental value (the "blue solutions" are a part of a standard general chemistry curriculum and are well known to practically every chemist). The study is elegantly designed, consistently executed and well written. However, the methodology is compromised due to seemingly small flaws, which are known to have dramatic effects on the quality of the results. Those include the choice of density functional with little amount of exact exchange and the use of the improper MD sampling technique (thermostat) to evaluate dynamic properties of the system. Experimental validation could in principle lift the doubts, but it does not provide any insights into the dynamic properties in question, whereas the agreement with theory is at most mediocre (see, in particular, Fig. 5, panel b). I will elaborate on both point below.*

*Therefore, keeping in mind the boost a publication in the Nature family enjoys, I can't recommend publication of this work in Nature Communications due to questionable data quality. I strongly believe that neither the importance of the problem, nor the quality of images and text should not justify sloppy methodology and seemingly insufficient understanding of the underlying simulation methods.*

*I would, nevertheless, consider reviewing a revision if the work is appended with some more proper calculations to validate the current approach. Those should be based on a different functional and thermostat.*

*Major methodological issues:*

*1) It is known since at least 2005 that density functionals with increased amount of exact exchange are more suitable for simulating solvated electrons. Those come independently from Herbert / Head-Gordon, Turi, Pasquarello, Lan / Rybkin to name a few. All these groups are unrelated and base their conclusions on different criteria (binding energies, dynamics, band structures, spin-densities as compared to wave functions etc.) Although GW is relatively independent of the DFT reference, it can't correct the trajectory propagated by PBE0 (with only 25% of exact exchange). In the case where (I cite the authors) "properties depend very sensitively on minor changes in molecular geometry and electron density" the choice of functional is critical, but here it is selected uncritically and against a well established consensus. Which different functionals have been used for which new calculations?*

**OUR RESPONSE:**

We thank the reviewer for pointing out the importance of density functionals with an increased amount of exact exchange. While our focus in the original manuscript was on the GW electronic structure, we do agree that the influence of the functional on the geometries generated by molecular dynamics should not be underestimated. In the revised manuscript, we consistently use the revPBE38-D3 density functional (which has a fraction of 3/8 of exact exchange) for both molecular dynamics and electronic structure analysis, together with careful benchmarking against GW. The original results for revPBE0-D3 are now presented only in the SI for reference and comparison. revPBE38-D3 shows electronic properties that are substantially closer to GW than those



from revPBE0-D3. This benchmark allows us to rely on revPBE38-D3 also for electronic properties, with the added benefit of better statistics due to the decreased computational cost. The comparison of the two density functionals shows that although the increased exact exchange fraction has a quantitative influence on the results, the conclusions and the overall behaviour of the system do not change.

2) *The authors (in the SI) allege to have used the Nose thermostat for production runs, actually referencing Nose and Hoover, but not the Nose-Hoover (NH) chain (or was in the chain?), this observation itself being telling. Deriving dynamic properties (such as the frequency of oscillation between the metallic and electrolyte states) is a typical and sad error. The NH and many other thermostats based on aggressive velocity rescaling dramatically distort particle dynamics and generally inapplicable for properties such as diffusion, vibrations and indeed fast state oscillations. A converged (sic!) NH trajectory can give us an equilibrium constant between the electrolyte and metallic states (in terms of time distributions). The information on their instant lifetimes and molecular mechanisms of transition are spurious. More to this, integrating several 1ps trajectories are a good strategy for probing dynamic properties with proper integrator (why not simply NVE or stochastic velocity rescaling?), but for the NH they are very far from convergence. That said, I believe that short-time fluctuations (main discovery of the work!) are very plausible, but I don't have to believe, it's science.*

OUR RESPONSE:

Following the reviewer's suggestion we have recalculated everything in the NVE ensemble to make sure that the dynamics we describe is not compromised by potential artifacts due to the coupling to the thermostat. The NVE results are now presented in the main text. At the same time, by comparing NVE and NVT simulations, we demonstrate in the SI that the introduction of the thermostat actually does not introduce any appreciable artifacts in this particular case. This is consistent with the fact that although formally dynamics should only be calculated from NVE trajectories, a suitable global thermostat often yields dynamical properties very close to NVE results.

3) *Experimental validation. The PE spectra (albeit with some assumptions) document the simultaneous presence of the species with and without band gap. However, they do not provide any insights in the dynamics properties (e.g. the oscillation time between the states). Although the presented picture explains the observation in general, no direct experimental support for is shown. Keeping in mind a very moderate agreement of the computed and experimental numbers, one should not rule out the possibility that a different model reaches a better agreement.*

OUR RESPONSE:

We agree with the referee that the measured photo-electron spectra do not give any insights into dynamical properties of the flipping. Our only aim was to use a characteristic quantity (or descriptor) that can not only be calculated accurately but also measured directly, i.e. no set of assumptions needs to be considered. We identified the DoS as this quantity. Furthermore, based on the new calculations we have now a clearer picture of the electronic structure changes which in fact allows a different interpretation. Taking also the other referee’s comments into account, we have re-written the section on experimental validation, vide *infra*.

## Reviewer 2

### Comments

*The manuscript by Jungwirth and co-workers presents an interesting perspective on solvated electrons in ammonia solutions. This work is a detailed continuation of their previous study on the gradual, non-first-order electrolyte-to-metal transition [Science 368, 1086-1091 (2020)]. Additionally, they found a rapid flipping between electrolyte and metallic states.*

*They have combined state-of-the-art hybrid functional-based molecular dynamics to obtain accurate dynamics and the GW method to accurately capture the electronic density of states of the solvated electron at various concentrations. The calculated density of states is further compared with experimental photoelectron spectroscopy. Overall, the manuscript is well-written, and the conclusion that both simulations and experiments evidence rapid flipping between electrolyte and metallic states is well-supported.*

*There are a few scientific issues that the authors need to address:*

*Regarding the calculations of DoS, are they all performed using GW methods? For instance, did the authors perform GW calculations for Figure 2 a, b? If the DoS are presented at different levels of theory, the authors should indicate the electronic structure theory used to obtain the DoS in the captions.*

OUR RESPONSE:

We thank the reviewer for this suggestion. In the current version of Figure 2, the DoS calculations were performed using the revPBE38-D3 functional, rather than  $G_0W_0$ . We have updated all figure captions to clearly indicate the electronic structure method used in each case.

*There is a follow-up question regarding the DoS, if Figure 2 is carried out using revPBE0 hybrid functional. In Section 4. Extended results in SI show the correlation between revPBE0 energies and the GW method for both orbital energy and band gap. revPBE0 with 0.25 HFX doesn’t rule out the self-interaction error. This is evident as revPBE0 overestimates the HOMO and underestimates the LUMO, resulting in a smaller band gap compared to the GW method. One needs to use a hybrid functional with a higher fraction of HFX, such as about*

40% HFX for water, which should fulfill the piecewise linearity of the functional upon fractional electron occupation[Phys. Rev. Research 3, 023182]. For its application to aqueous electrons, see [J. Phys. Chem. Lett. 2017, 8, 9, 2055–205] and [Angew. Chem. Int. Ed. 2022, 61, e202209398 ]. If one extrapolates the correlations between revPBE0 and GW band gap (Figure 4 a in SI), we can see that when the revPBE0 gap decays to 0, the GW still predicts a band gap of around 0.3 eV. Although the picture of flipping between electrolyte and metal might not change, the analysis of the 3.0 MPM would be less accurate. It may likely be only electrolyte, or at least less metallic.

OUR RESPONSE:

This issue has been already addressed above in our response to Reviewer 1

## Reviewer 3

### Comments

*The authors present a computational study of lithium ammonia solutions across a concentration range of the electrolyte-to-metal transition in the corresponding solutions. They use ab initio molecular dynamics simulations based on a DFT approach to describe the dynamics of the system and calculate the density of states at selected snapshots. Furthermore, they calculate a spherical band structure to address the dispersion relation of electrons in these disordered liquid systems, and to better describe the band gap of these systems. For the latter task they use a specially developed computational tool. To verify their computational results, they compare their results to experimental photoelectron data obtained from previously published but re-evaluated liquid jet measurements.*

*They find, that with increasing metal concentration, the band gap of the system closes and fills, in agreement with a gradual electrolyte-to-metal transition. Most remarkably, they observe ultrafast flipping of the system between electrolytic and metallic behaviour on timescales of 40 fs in the intermediate concentration regime, over which the gradual transition to the metallic phase occurs. This flipping behaviour, is attributed to minor changes in the molecular structural arrangement of the liquid, that can drastically change the electronic structure. They relate the observed temporal fluctuations of the electronic structure to previously observed spatial inhomogeneities and concentration fluctuations in alkali ammonia solutions of intermediate concentration.*

*I believe such studies are important in providing a deeper molecular level understanding of the fascinating behaviour of alkali ammonia solutions and their transition to a liquid metallic phase. Experimental studies alone, usually are not able to deliver such detailed molecular level insights. I believe the study is sound the results are novel and in principle well suited for publication in nature communications.*

*However, there remain a few open questions regarding the connection of the*

observed flipping between states and the transition to the metallic state as well as regarding the comparison between experimental data and computational results that, in my opinion, need to be addressed prior to publication.

1. While the finding of fluctuations between electrolytic and metallic states is fascinating, it does not become absolutely clear to me how this behaviour relates or contributes to the transition of the metallic phase. Can these fluctuations of the band structure with time really directly be connected to the spatial inhomogeneities and concentration fluctuations described in the introduction (bottom half of second column, page 1)? After all, the simulations in a small cell of 15 Å, with a fixed number of ammonia molecules and lithium atoms can not show fluctuations of the concentration? It could be helpful to more clearly explain the connection between these observations and the observed temporal fluctuations.

OUR RESPONSE:

Earlier studies by Jortner et al. predicted that the size of the spatial inhomogeneities in the present systems will be of the order of units of nanometers. The chosen unit cell corresponds roughly to this size and represents sort of a sweet spot. Simulating a much larger unit cell would not only become computationally unfeasible but would also provide averaged results over metallic and electrolyte domains rather than flipping between them, as investigated in the present study. This is now explained in more detail than before in the main text of the revised ms.

2. For the gradual transition to the metallic phase, it would be very interesting to see a direct comparison of the situation at various intermediate concentrations. While this is provided in figure 1 for some quantities it seems to be missing for some others.

a. For example, the change of the spatial extent of the dielectrons (radius of gyration and Wannier orbitals) changes drastically between 3 and 6 MPM, with a much-decreased difference between metallic and electrolytic configurations at 6 MPM. Are these effects understood?

b. the charge carrier mobility seems to significantly decrease for the metallic states of 6 MPM vs those at 3 MPM. Is this effect understood? c. For a gradual transition to the metallic phase I would have expected that at 6 MPM the system spends more time in metallic states than in the 3 MPM case, but this seems not to be the case. Do they authors understand why? I think these effects could and should be mentioned and possibly explained in the main text.

OUR RESPONSE:

Following the reviewers suggestion we now present in the main text of the revised manuscript results for 4 systems of increasing electron concentration (3.0, 6.0, 11.1, and 13.5 MPM). Moreover, with the new calculations employing a hybrid DFT functional with a larger fraction of exact exchange, we observe (as expected) a monotonous increase of metallicity with concentration.

Regarding the change in the spatial extent of dielectrons, as shown in Figure

3 of the main text and SI Figures S14, S15, S21, S22 and S23 we observe that the gyration radii decrease from 3.0 to 6.0 MPM due to mutual repulsion and stabilization by  $\text{Li}^+$  cations. At higher concentrations (11.1 and 13.5 MPM), electron-electron repulsion promotes delocalization, leading to a coexistence of localized and delocalized states. For 6.0 MPM, the state of the system—metallic or electrolyte—is determined as a whole, based on the bandgap and conductivity. Since the system contains two dielectrons, it is not feasible to correlate the gyration radii of individual dielectrons to the system’s state. One dielectron may be more localized (with a smaller gyration radius), while the other may be more delocalized (with a larger gyration radius), with the latter likely contributing to the system’s metallic conductivity. However, the overall state reflects the combined behaviour of both electrons.

In comparing the old results obtained with revPBE0-D3 and the new results with revPBE38-D3, we note a few key differences. For the 6.0 MPM system, revPBE0-D3 calculations revealed a clear distinction in gyration radii between metallic and electrolyte states, which is less pronounced in the revPBE38-D3 results. This may be attributed to the higher fraction of exact exchange in revPBE38-D3, which reduces the contrast between metallic and electrolyte states at intermediate concentrations.

Regarding the charge carrier mobility, the trends observed also differ between the two functionals. For revPBE38-D3, we observe a monotonic increase in conductivity with increasing electron concentration, consistent with a gradual transition to metallicity. In contrast, the revPBE0-D3 results show an initial decrease in conductivity from 3.0 MPM to 6.0 MPM, followed by an increase at 11.1 MPM. We currently cannot attribute this drop in conductivity at 6.0 MPM to a specific mechanism.

It is important to note that these analyses rely on relatively small samples based on correlated 1 ps trajectories consisting of 500 snapshots per concentration and functional. This limited sample size constrains our ability to draw definitive conclusions, and we are cautious not to overinterpret these findings.

*3. A brief comment on how the 100 frames for the band structures in figure 1 are selected would be helpful. Do these band structures only contain metallic frames or also electrolytic frames?*

OUR RESPONSE:

We appreciate the reviewer’s question regarding the frame selection process. In the current version of the manuscript, we used a randomly selected 1 ps segment of the trajectory, from which 100 frames were sampled at 10-fs intervals. This segment includes both metallic and electrolyte frames, providing an average over both states.

*4. The method to separate the non-metallic photoelectron signals from the*

*metallic ones for the 3.4 MPM photoelectron spectrum has not been reported in the prior publication (reference 5 in the main text), so this should be explained here. I assume it is based on the fitting procedure, which allows subtraction of the plasmon signals and subsequent creation of a type of masking filter to separate the strongly overlapping photoelectron bands corresponding to the metallic and electrolytic solvated electrons (figure 4 of reference 5), is this correct?*

OUR RESPONSE:

Referee 3's assumption is correct. To elaborate further – we agree with Referee 3 that the method of how to separate the non-metallic photoelectron (PE) signals from the metallic ones for the 3.4 MPM photoelectron spectrum has only been reported briefly in the main text. We now give the full quantitative analysis the supplementary information (SI) with a link to the SI in the main text. In a nutshell, at  $\sim 0.35$  MPM we characterized the solvated di-electron peak, while at  $\sim 9.7$  MPM we observed a fully metallic PE spectrum at  $\sim 9.7$  MPM consisting of a conduction band with a sharp Fermi-edge and the plasmon peak progression, which were both fitted to a free-electron gas model. The aim of this analysis was to quantify for intermediate concentrations within the gradual electrolyte-to-metal transition the ratio of PE spectral features originating from solvated (di)electrons versus metallic ones.

*5. I find the comparison of the computational results to the experimental data not fully convincing:*

*a. I find that the representation of the experimental signals without vertical axis scale is misleading. In reference 5 of the main text (i.e. the initial publication of the experimental work) it looks like the experimental signals for the electrolytic and metallic states are of very similar intensity, yet in figure 5 they are scaled very differently (panels b and c), as if the metallic photoelectron signal would only correspond to the very low calculated density of states close to the Fermi level. If this is the case, the largely different relative magnitudes may indicate a significant disagreement between the calculations and the experimental data, that would need to be addressed.*

OUR RESPONSE:

First, let us address here two experimental properties which can drastically influence measured intensities of photo-electron (PE) signals: (i) we do not know the ionization cross sections in conjunction with the detection efficiency of the used experimental setup. It is well possible, that the ionization cross sections as well as the anisotropy parameters differ significantly between the free electrons of the conduction band and the localized solvated di-electrons. (ii) PE spectroscopy is a surface sensitive method, which means that if free-electrons or solvated di-electrons tends to be more surface active than the other species we would detect them with higher intensity. These two experimental issues make it difficult to compare calculated and measured absolute intensities. Thus, we focus on comparison of the energetic positions of the computed DoS as well as their shapes, while comparisons of absolute intensities are beyond the scope of

the present study.

*b. Also in the conclusion they refer to this point again: "Moreover, we demonstrate that the densities of states of metallic configurations still to a large extent possess features pertinent to electrolyte configurations, with only a weak filling of the band gap." In my opinion this contradicts the experimental data in reference 5, which shows photoelectron signals rising toward Fermi level and a sharp band edge.*

OUR RESPONSE:

The points raised by Referee 2 may be addressed by the explanations of the previous point. We, however, agree with Referee 2, while also including points of Referee 1 and 3, that the comparison and the discussion of the measured photo-electron data and the newly calculated DoS should be re-evaluated not only to clarify points raised by all three referee but also to point out the differences to previous interpretations and potentially new insights from gained from the presented simulations. To this end we modified large parts of the whole section 'C. Experimental Validation' and took the liberty to extend the text a bit in order to clarify any potentially misleading points.

*c. Interestingly the calculated density of states for the metallic configurations in the 3 MPM case (panel a), shows also a bimodal structure in the lower energy peak (not visible in panel b due to the scaling). However, the authors do neither address this in the text, nor compare it to the experimental data.*

OUR RESPONSE:

See our response to the previous point.

*Minor comments:*

*1. It would be helpful to refer the reader to explicit sections in the SI, rather than referring the reader to the SI as a whole. It always took me some time to find the information relevant at a specific point of the main text.*

OUR RESPONSE:

The reader of the main ms. is now always referred to specific sections of the SI

*2. In the supplementary information, in the comparison of the ammonia 3a1 density of states to the photoelectron data (figure 11) it does not become clear to me which features the authors think agree and which disagree. Do they assume all the fine structure is real? In reference 5 of the main text (i.e. the original publication of the experimental data) the changes to the 3a1 band are described as a broadening and shift towards lower binding energy. In the representation in figure 11 I cannot clearly see this effect, or at least cannot judge if the calculations reproduce this effect.*

OUR RESPONSE:

We have now added a separate Figure S13 in the SI which illustrates the broadening of the  $3a_1$  orbital of liquid ammonia more clearly upon increase of lithium concentration from 3.0 to 13.5 MPM. In the experiment, the broadening is more difficult to quantify since the much more intense gas phase peak does not allow to determine the width of the  $3a_1$  peak, however, we observe a similar tendency.

*3. There exists a significant number of studies of solvated electrons in alkali-doped clusters of ammonia and other solvents, also covering a wide concentration range (not cited in the current manuscript). In the past it has been questioned if such studies can show bulk like electronic structure features, due to their limited system size. The system calculated here (64 ammonia molecules with up to 10 Li atoms) is comparable to the cluster systems studied experimentally. Is it clear that in the calculation the system size is big enough to predict bulk properties? If so, is there a clear argument that this is the case?*

OUR RESPONSE:

The reviewer has a point in that for the employed unit cell there may be artifacts due to the limited system size. However, the issue is less severe here for concentrated solutions as compared to simulations of a single solvated electron. Moreover, studies of analogous salt solutions (see, e.g., Phys. Chem. Chem. Phys., 2012,14, 10248-10257) examined size effects on structural properties finding that for chosen unit cell size such artifact are only of a minor importance.

*4. Since the flipping between the electrolytic and metallic states is driven by minor changes to the molecular arrangement, the temperature of the sample should have an effect on the frequency of the flips. A full analysis of this temperature dependency is likely beyond the scope of this work, but it would be worth to state the simulated temperature of the system at some point in the main text.*

OUR RESPONSE:

The NVE simulations presented in the revised ms. correspond to a mean temperature of 235 K. Performing additional simulations at different temperatures goes beyond the scope of the present study. It may provide some additional information on the frequency of the metal/electrolyte flips, however, at the cost of multiplying severalfold the (already high) computational expenses.



# **Reply to reviews for:**

## Rapid flipping between electrolyte and metallic states in ammonia solutions of alkali metals

January 21, 2025

**Dear editors,**

thank you for considering the revised version of our manuscript “Rapid flipping between electrolyte and metallic states in ammonia solutions of alkali metals” for publication in Nature Communications. We are glad that all three reviewers appreciated the revisions we made and that the first two reviewers are fully satisfied with the revised version of the ms. Below, we address in detail the remaining point raised by Reviewer 3 concerning comparison between the calculated and experimental photoelectron spectra (our response to this issue is shown in [blue](#)).

### **Reviewer 3**

#### **Comments**

As expressed in my previous comments, I believe the presented computational study reveals new insights into the molecular level properties of alkali solutions in liquid ammonia, specifically into the mechanisms driving the electrolyte to metal transitions at high alkali concentrations. I believe this study is in principle well suited for publication in Nature Communications. The authors have addressed most of my questions and concerns. There is in fact only one point that I think the authors did not address adequately, which is related to the comparison between their calculated DoS and the previous experimental results from liquid jet photoelectron spectroscopy (figure 5 in the main text).

I do not agree with the authors in their overall assessment, that “The general agreement between the computational and experimental time-averaged results thus demonstrates the effectiveness of the employed computational methodology, while also providing detailed insights into the electronic structure changes occurring during the EMT.”

The only agreement I can see in figure 5 b and c is that the DoS of the metallic frames and the signal corresponding to conduction band electrons is non-zero

at the Fermi level, while the DoS of the electrolyte frames and the experimental signal corresponding to solvated dielectrons is not. Given the previous sections of the manuscript, and the analysis of the experimental data, this would however be a rather trivial statement. The overall shape of the DoS is however completely different. In addition, the position of the DoS feature corresponding to the solvated dielectrons agrees with their experimental counterpart.

Claiming agreement in the Fermi edge region in figure 5 c, after rescaling the calculated metallic frame DoS (by what I estimate to be more than one order of magnitude) seems misleading to me. Claiming agreement in panel 5 b, between the electrolytic DoS and the experimental dielectron signal is possible, but the agreement with the metallic frame DoS or total (averaged over all frames) DoS would likely be similar.

I think there is a strong discrepancy between the calculations and the experimental data concerning the very low DoS at the Fermi level for the metallic frames, while the experimental data indicates equal intensity for conduction band electrons and solvated dielectrons. The authors comment on the fact that the DoS for metallic frames still shows a strong contribution of localized solvated dielectrons, making the comparison to the decomposed experimental data challenging. This seems to be a valid and interesting conclusion, but still the observed density of localized solvated dielectrons and delocalized conduction band electrons seems to disagree between experiment and calculation. A similar observation can be made in figure 5 d for the high alkali concentrations: At the Fermi level, the calculated DoS is much lower than indicated by the photoelectron signals. This disagreement for me seems to be the most important (and interesting?) observation from the comparison in figure 5.

In their reply to my previous comment regarding this, they give possible explanations for these discrepancies:

1. Possible differences in the photoionization cross sections and photoelectron angular distributions of conduction band electrons and solvated dielectrons
2. Possible differences in the surface activities of the different electronic species.

While this does not immediately seem very likely to me, the authors should discuss these possibilities in the main text, if they believe these points can explain parts of the observed discrepancies. Is there other possible (experimental or computational) explanations for the discrepancies? Would it not be better to compare the calculated DoS averaged over all frames with the complete experimental photoelectron spectrum? Decomposing the photoelectron spectrum into localized and delocalized electrons seems unnecessary given the fact that also the metallic frames show still a substantial content of localized solvated dielectrons.

At the moment the comparison offered in figure 5, with the claim of agreement rather than discussion of possible origins of the discrepancies between calculations and previously reported experiments in my opinion weakens this

overall strong manuscript considerably, and I believe this part should be improved prior to publication.

OUR RESPONSE:

Concerning the last remaining issue raised by Reviewer 3, i.e., the benchmarking of calculated vs experimental time-independent photoelectron spectra we decided to yield to the Reviewer by removing the whole contentious sentence "The general agreement between the computational and experimental time-averaged results thus demonstrates the effectiveness of the employed computational methodology, while also providing detailed insights into the electronic structure changes occurring during the EMT." Instead, we now discuss in further detail and in a more sober tone the comparison between calculated and measured spectra, rationalizing the existing discrepancies primarily in terms of necessarily different ways of spectral decomposition into electrolyte and metal contributions for the two approaches. Additionally, we have restructured this section so that we start with a comparison of the total signals at the high (metallic) concentration, followed by a discussion of the intermediate concentration with decomposition to metallic and non-metallic frames (with the figure with total signals — asked for by the Reviewer — presented and discussed in the SI section 4.1).

**Reply to reviews for:**  
Rapid flipping between electrolyte and metallic  
states in ammonia solutions of alkali metals

February 14, 2025

**Dear editors,**

thank you for considering the revised version of our manuscript “Rapid flipping between electrolyte and metallic states in ammonia solutions of alkali metals” for publication in Nature Communications. We appreciate the constructive feedback from Reviewer 3 and acknowledge their remaining concerns regarding the comparison between the calculated and experimental photoelectron spectra. In this revision, we have carefully addressed all points raised and made changes to ensure a more direct and transparent comparison. Below, we detail our response (highlighted in [blue](#)).

**Reviewer 3**

**Comments**

I think the changes the authors made are moving in the right direction, but they have only addressed a part of the concerns I have formulated. They did barely change the discussion of the case of 3.0/3.4MPM. My apologies if these concerns were not formulated clearly enough before:

The comparison between experimental data and calculation for the intermediate concentration range seems dishonest to me. I understand that the binary decomposition of the experimental data is the only way to separate “metallic signals” from “electrolytic signals”. Experimentally these signals at 3.4 MPM concentration are roughly equal in intensity (as is clearly seen in the corresponding plots in the SI). The calculation at a similar concentration shows roughly ten times the DoS at binding energies corresponding to solvated (di)electrons than at binding energies corresponding to metallic conduction band electrons (as can be seen from the various lines in figure 5 c).

I cannot understand how this is only an “apparent” discrepancy. The picture given by the calculations is maybe more nuanced, but certainly is different.

The separation of “metallic” and “electrolytic” experimental electron signals for me seems to hide the fact that the two have (experimentally) the same intensities. Of course, the experiment cannot separate metallic frames from electrolytic frames, making the comparison imperfect. But the computational results can easily provide the information corresponding to the experimental results: What is the DoS at binding energies corresponding to solvated (di)electrons and what is the DoS corresponding to conduction band electrons close to the Fermi edge. This would correspond to the comparison of the sum of experimental signals of metallic and electrolytic electrons (total electron signal minus the plasmon signals) to the calculated density of states (total or only metallic frames), similar to the comparison the authors show in figure 5a for the purely metallic case.

In other words: The separation of the experimental signal into “electrolytic” and “metallic” electrons, does not make any sense for me. Instead their sum should be compared to the calculated DoS, and the discrepancies explained (photoionization cross sections? Surface activity of different electronic species etc?).

I think this comparison should be given in figure 5 and discussed. As this comparison is not the main finding of this manuscript, I do not believe that there needs to be perfect agreement between calculations and experiments, but the comparison needs to be fair.

#### OUR RESPONSE:

We acknowledge the reviewer’s concerns regarding the comparison between experimental and computational results at intermediate concentrations and follow their suggestion. Namely, in order to fully address the issue in the main text, we now explicitly present in Figure 5b and discuss in the ms. the calculated total time-averaged DoS (green) at 3.0 MPM compared directly with the time-averaged experimental PE signal (grey) at 3.4 MPM. This provides a direct unbiased comparison between theory and experiment, before any decomposition into electrolyte and metallic components.

We retain the decomposition into electrolyte-like and metallic-like states (Figures 5c and 5d) in order to provide additional insight into the nature of the electronic states in the simulations. We now explicitly acknowledge in the main text that the experimentally observed spectral intensities of electrolyte and metallic states at 3.4 MPM are approximately equal, while in the calculations, the DoS at binding energies corresponding to solvated (di)electrons is significantly larger than the DoS at binding energies near the Fermi level. This discrepancy is no longer described as merely “apparent” and we instead discuss

possible explanations for this difference.

We now suggest that the discrepancy may partially stem from differences in photoionisation cross sections or variations in the angular distribution anisotropies of the emitted photoelectrons originating from localised (di)electrons vs. delocalised metallic electrons. Also, the sensitivity of the experimental technique may differ for localised vs. delocalised states, potentially affecting their relative intensities.

In summary, in line with the reviewer’s recommendation, we have moved the comparison of total signals for the intermediate concentration from the SI to the main ms. and extended&revised the corresponding discussion to provide a transparent and balanced interpretation of the comparison between experiment and calculations.