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Frontier orbitals and quasiparticle energy levels in ionic liquids

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Ionic liquids (ILs) are salts formed of molecular cations and anions that exist in the liquid state at or near room temperature. They find widespread use as solvents, disperants, and electrolytes, and exhibit several unusual properties, including high electrochemical stability windows and very low equilibrium vapor pressures. From a fundamental point of view, it is important to understand the character of the frontier molecular orbitals and determine their quasiparticle energy levels in ILs, as these determine technologically important properties, such as band alignment at interfaces, reactivity, and stability with respect to electron injection or removal. In recent years, a number of experimental and theoretical investigations of the electronic structure of ILs have been reported. For example, photoelectron spectroscopy has been used to study the valence band electronic structure of liquid ILs and IL vapors consisting of neutral cation–anion pairs.

To gain a detailed understanding of the properties of ILs, many groups have carried out calculations based on density-functional theory (DFT). To model photoemission experiments, several studies compared the Kohn–Sham (KS) eigenvalues obtained from DFT calculations to the measured photoelectron spectra. This practice is based on the observation that in many materials KS eigenvalues can be useful approximations to quasiparticle energies that are measured in photoemission spectroscopy. However, it is well known that the quantitative agreement between KS eigenvalues and quasiparticle energies often depends sensitively on the choice of exchange–correlation functional. In recent years, several DFT-based approaches, including Koopmans’ corrected functionals, ranged-separated hybrid functionals, or dielectric dependent functionals, have been developed that can produce good agreement between KS eigenvalues and quasiparticle energies. Despite this, many DFT studies of the electronic structure of ILs employ simpler exchange–correlation functionals, such as semilocal or traditional hybrid functionals.

Moreover, it is well known that KS eigenenergies cannot be rigorously interpreted as quasiparticle energies (with the exception of the energy of the highest occupied molecular orbital (HOMO), which are measured in photoemission spectroscopy. True quasiparticle energies of all occupied and empty states can be obtained from Green’s function techniques, such as the GW approximation.

In this work, the GW method is used to study the electronic structures of ILs. As a case study, the electronic structure of the 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF4]) ion pair is analyzed in detail with a focus on the nature of the frontier molecular orbitals in this system. Calculated quasiparticle energies from G0W0 calculations are also compared against recent photoemission measurements of several different ILs. In particular, gas phase spectra of IL vapors are compared against simulated spectra of free ion pairs, and liquid phase spectra of ILs are compared against theoretical calculations of periodic crystalline ILs. In all cases, excellent agreement between measured photoemission spectra and GW calculations is found, while DFT results depend sensitively on the treatment of exchange–correlation effects.

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RESULTS

[EMIM][BF₄] ion pair

We first consider the electronic structure of the [EMIM][BF₄] ion pair (Fig. 1). Figure 2 shows the calculated densities of states (DOS) of the [EMIM][BF₄] ion pair from different levels of theory. The leftmost column contains results from three different mean-field methods: HF, DFT with the PBE0 functional, and DFT with the Perdew–Burke–Ernzerhof (PBE) functional. The Mulliken decomposition of the total DOS into cation and anion contributions is also shown. The three curves exhibit significant quantitative and qualitative differences. For example, while PBE predicts that the HOMO orbital is centered on the anion, PBE0 and HF place the HOMO orbital on the cation and the associated HOMO energies differ by several electron volts among the different approaches. To illustrate this point further, isosurface plots of the HOMO-1, HOMO, and LUMO orbitals are shown in Fig. 3. The three leftmost columns show that PBE, PBE0, and HF predict three different sets of frontier orbitals in this system. In particular, all three frontier orbitals are localized on the [EMIM] ion in HF, while the HOMO-1 in PBE0 and PBE is on the [BF₄] ion. In PBE, the HOMO is also localized on [BF₄]. These results demonstrate the difficulty of answering questions about the nature and energies of the frontier orbitals in ILs based on energy eigenvalues and orbitals from mean-field approaches.

Calculated DOS from G0W0 and eigenvalue self-consistent GW (evSCGW) calculations are shown in the middle and rightmost columns of Fig. 2. Already at the G0W0 level, the dependence on the mean-field starting point is significantly reduced and all G0W0 results predict that the HOMO orbital lies on the [EMIM] cation. The starting point dependence is even weaker in the evSCGW calculations con...
are shown in Fig. 4. In both cases, excellent agreement between spectra, i.e., both the absolute and the relative binding energies of or calibrations of any kind have been applied to the theoretical theory and experiment is observed. We emphasize that no shifts of that subshell at the relevant photon energy51. Uniform Gaussian broadening has been applied to each theoretical spectrum.

We next compare GW results for different ion pairs to experiment. The simulated spectrum is a sum of atomic orbital projected DOS (pDOS) curves, each weighted by the per-electron photoionization cross-section spectrum. As discussed above, see Fig. 5. In particular, peaks A, B, and D’ are missing from the simulated spectrum, and the intensity ratios of peaks D, E, and F are different from the experimental ones. In previous studies, it has been observed that the two ions of the [EMIM][BF₄] ion pair can react to form an adduct upon heating52,53. Figure 6 shows the structure of the adduct. To assess whether adduct formation is responsible for the differences between the simulated and the measured spectra, we performed GW calculations on the adduct. We then added the adduct spectrum to the ion pair spectrum assuming that the vapor is a 1.5:1 mixture of ion pairs and adducts. Figure 5 shows that the resulting spectrum is in much better agreement with the measurement. In particular, peaks B and D’ are present and the intensity ratios of peaks D, E, and F are correct, but peak A is still missing.

Table 1. HOMO and LUMO levels of the [EMIM][BF₄] ion pair from different levels of theory.

| Method     | HOMO/–first IE | LUMO/–E.A. | Gap     |
|------------|----------------|------------|---------|
| PBE        | −6.80          | −1.99      | 4.81    |
| PBE0       | −8.44          | −1.01      | 7.43    |
| HF         | −10.60         | 1.89       | 12.49   |
| G0W0@PBE   | −10.44         | 0.23       | 10.67   |
| G0W0@PBE0  | −10.51         | 0.49       | 11.00   |
| G0W0@HF    | −11.03         | 1.28       | 12.31   |
| evSCGW@PBE | −11.14         | 0.80       | 11.94   |
| evSCGW@PBE0| −10.79         | 0.79       | 11.58   |
| evSCGW@HF  | −11.03         | 1.23       | 12.26   |
| ΔSCF@PBE   | −9.55          | 0.43       | 9.98    |
| ΔSCF@PBE0  | −10.20         | 0.58       | 10.78   |
| ΔSCF@HF    | −9.10          | 1.43       | 10.53   |
| ΔCCSD(T)   | −10.49         |            |         |
| Experiment | −10.4          |            |         |

All energies are given in eV.

*Peak C in the UPS spectrum (Fig. 5).

Ion pairs: theory vs. experiment
We next compare GW results for different ion pairs to experimental photoelectron spectra of IL vapors. The simulated spectra are constructed from G0W0 calculations with a PBE0 starting point based on the “Gelius approximation,” i.e., the spectrum is a sum of atomic orbital projected DOS (pDOS) curves, each weighted by the per-electron photoionization cross-section of that subshell at the relevant photon energy51. Uniform Gaussian broadening has been applied to each theoretical spectrum.

In the condensed phase
Finally, we also carry out GW calculations of ILs in the condensed phase and compare them to experimental photoelectron spectra. In principle, the simulated spectrum of the IL should be obtained by averaging results of different liquid configurations. However, performing many GW calculations of large unit cells is computationally extremely challenging. Instead, we instead carry out GW calculations on ILs in a solid, crystalline phase. This approximation is justified as the internal structures of the ions and their average coordination environments are similar in the solid and liquid phases. Figure 7 shows the unit cells of the three crystalline ILs 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]), [EMIM][BF₄], and 1-butyl-3-methylimidazolium chloride ([BMIM] Cl) and also compares the simulated G0W0@PBE0 spectra to experimental photoelectron spectra taken in the liquid phase. In photoemission measurements of liquids and solids, the experimental binding energies are given relative to the Fermi level, but
since the position of the Fermi level relative to the band edges is not known a priori, the calculated spectra have been shifted by a constant amount to best match the experiment. Excellent agreement between theory and experiment is found for [BMIM][PF₆] and [EMIM][BF₄]. In the case of [EMIM][BF₄], peaks I and II are correctly reproduced, which is an improvement over previous DFT results¹⁵. In the spectrum of [BMIM]Cl, the separation between the two most intense peaks (peaks I and IV) is overestimated by approximately 1.3 eV, but otherwise the measured spectrum is reproduced with good accuracy. The results shown in Figs. 4 and 7 demonstrate that the GW method is very well suited for predicting quasiparticle energy levels in ILs and free ion pairs.

**DISCUSSION**

An alternative method for modeling photoelectron spectra of ILs based on DFT was proposed in ref. ⁵⁴. In this study, it was shown that experimental spectra of liquid ILs can be reconstructed from DFT partial DOS curves of free ion pairs by shifting the cation and anion partial DOS curves relative to each other by an amount that is determined on a case-by-case basis. The size of these shifts was originally interpreted as the difference between the average electrostatic potentials experienced by the cation and the anion. Our GW results, however, suggest that this interpretation needs to be revised. In particular, Fig. 2 shows that the GW self-energy corrections give rise to a significant relative shift of the anion and cation partial DOS curves. This shift does not arise from electrostatic effects but instead from a more accurate treatment of exchange and correlation effects. Therefore, the shifts applied in ref. ⁵⁴ do not arise solely from electrostatic effects and should be interpreted as empirical corrections that contain contributions from both self-energy effects and changes in average electrostatic potential.

Detailed knowledge of the character of the frontier molecular orbitals and their quasiparticle energies is of crucial importance for understanding the electronic structures of ILs. In this study, we have shown that interpreting DFT KS eigenvalues as true quasiparticle energies can lead to qualitatively and quantitatively inaccurate results. This problem can be overcome by the GW method which produces results that are in excellent agreement with state-of-the-art photoemission data. These results suggest that the GW method is a useful tool for studying the electronic structure of ILs and can be used to gain insights into electronic properties that are relevant to IL devices, such as band alignment at interfaces and stability with respect to electron injection and removal.

**METHODS**

Electronic structure calculations

All HF, DFT, and GW calculations reported in this work were performed using the FHI-aims electronic structure program⁵⁵–⁵⁷ that uses atom-centered local basis functions defined on a numerical grid. The geometries of the free ion pairs were relaxed using DFT with the PBE0 exchange–correlation functional until the forces on the atoms were <0.005 eV/Å. van der Waals (vdW) interactions were accounted for using the Tkatchenko–Scheffler method⁵⁸,⁵⁹. For each ion pair, a number of different configurations were manually constructed, and in the end the relaxed geometry with the lowest energy was used for the DOS calculations. The default “tight” numerical basis sets were used during...
the geometry optimizations. For the bulk crystals, the calculations were performed at experimental geometries from X-ray crystallography \(^5^9,^6^0\). The implementation of the GW method in FHI-aims is described in ref. \(^6^1\). The self-energy was calculated on the imaginary frequency axis with 100 frequency points, and the Pade approximation with 16 fitting parameters was used for the analytical continuation of the self-energy onto the real axis. For the G0W0 and evSCGW calculations, the NAO-VCC-nZ basis sets were used (NAO-VCC-4Z for the ion pairs and NAO-VCC-3Z for the bulk solids) \(^6^2\). All of the occupied and empty electronic states spanned by the basis sets were included in the GW calculations. A graph showing basis set convergence is included in the Supplementary Information. The bulk calculations were performed at the Gamma point only. The GW calculations were performed on the UK’s national supercomputer Archer. The calculations of the free ion pairs were run on 8 nodes (192 processors in total) and a typical G0W0 calculation took approximately 4 h. The calculations of the bulk solids (approximately 100 atoms per unit cell) were run on 64 nodes (1536 processors in total) and a typical G0W0 calculation took approximately 13 h. CC calculations for determining the vertical first ionization energy of the [EMIM][BF \(_4\)] ion pair were performed using NWChem\(^6^3\). The geometry relaxed at the PBE0 + vdW level of theory was used. The total energies of the neutral ion pair and the ion pair cation were calculated at the CCSD(T) level of theory, using cc-pVTZ (correlation-consistent, valence triple zeta with polarization functions) basis sets \(^6^4\).

**DATA AVAILABILITY**

The structures of all of the ion pairs and solids considered in this work are given in the Supplementary Information.

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COMPETING INTERESTS
The authors declare no competing interests.

ADDITIONAL INFORMATION
The online version of this article (https://doi.org/10.1038/s41524-020-00413-4) contains supplementary material, which is available to authorized users.

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