Optical response of the sodium alanate system: GW_0 -BSE calculations and thin film measurements

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We calculate from first principles the optical spectra of the hydrides in the sodium alanate hydrogen storage system: NaH, NaAlH₄, and Na₃AlH₆. In particular we study the effects of systematic improvements of the theoretical description. To benchmark the calculations we also measure the optical response of a thin film of NaH. The simplest calculated dielectric functions are based upon independent electrons and holes, whose spectrum is obtained at the G_0W_0 level. Successive improvements consist of including partial self-consistency (so-called GW_0) and account for excitonic effects, using the Bethe-Salpeter equation (BSE). Each improvement gives a sizable blue shift or red shift of the dielectric functions, but conserves the trend in the optical gap among different materials. Whereas these shifts partially cancel at the highest (GW_0 -BSE) level of approximation, the shape of the dielectric functions is strongly modified by excitonic effects. Calculations at the GW_0 -BSE level give a good agreement with the dielectric function of NaH extracted from the measurements. It demonstrates that the approach can be used for a quantitative interpretation of spectra in novel hydrogen storage materials obtained via, e.g., hydrogenography.

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I. INTRODUCTION

In recent years complex hydrides have attracted much attention due to their potential for use as hydrogen storage materials.^{1–3} Those consisting of light elements in principle allow for high gravimetric and volumetric hydrogen densities. The first complex hydride system consisting of light elements that was shown to be able to reversibly desorb and absorb hydrogen is based on sodium alanate. The desorption occurs in two steps, according to

Although the storage densities are insufficient, the first reaction, when doped with titanium, exhibits the desired thermodynamic and kinetic characteristics for operation in combination with a PEM (proton exchange membrane) fuel cell and is still the best performing complex hydride system today.⁴ Indeed this system has become a model system in the actively ongoing search for even lighter complex hydrides. Complex metal hydrides have a wider potential than hydrogen storage. In the future some may also be used in solar cell devices and lithium ion battery technologies.^{5,6}

Recently the new optical technique of hydrogenography was developed to systematically measure the thermodynamics of hydrogen desorption reactions.⁷ A vast range of hydrides

with a continuous composition gradient containing up to six different elements can be investigated in a single experiment. Hydrogenography is based on the fact that the electronic structure, and hence the optical properties, changes drastically when hydrogen is incorporated into a material. Analysis of the vast amount of data would be greatly facilitated if the optical spectra of the compounds involved were known. Computations yielding realistic spectra are needed.

Optical spectra of (complex) metal hydrides have been calculated at the independent electron and hole level, often based upon single-particle spectra calculated with GW in order to start from a reasonable band gap.^{8–18} Usually, a simple version of the GW approximation, which neglects effects of self-consistency, has been applied. Moreover, interactions between electrons and holes, giving rise to so-called excitonic effects, have been commonly neglected. In this paper we study the optical response of the hydrides in the archetypal complex hydride system of sodium alanate. By successive systematic improvement of the approximations we calculate the influence of self-consistency and excitons on the dielectric functions.

In order to test the calculations we measure the optical response of a polycrystalline thin film of sodium hydride (NaH) deposited on a quartz substrate as a function of frequency. The reflectance and transmittance spectra are used to extract the dielectric function of NaH. We show that good agreement between the experimental and computational results is obtained at the GW_0 -BSE (Bethe-Salpeter equation) level of approximation. In particular the importance of excitonic effects on the shape of the spectrum is demonstrated.

This paper is organized as follows. Section II outlines the computational methods. Section III discusses and presents the results of the optical experiment on thin film NaH. In Sec. IV computational results on the dielectric functions are presented, discussed, and compared to experiment. Section V summarizes the main conclusions.

II. COMPUTATIONAL METHODS

Density functional theory (DFT) calculations generally give good results for ground-state properties, but not for excited states. The electronic band gap, for instance, can be underestimated by $\sim 50\%$. This stems from an unjustified interpretation of the Kohn–Sham (KS) eigenvalues as single-particle excitation energies. The latter can be obtained from the quasiparticle (QP) equation, which involves the nonlocal, energy-dependent self-energy Σ ,

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) \right] \psi_{n\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; \epsilon_{n\mathbf{k}}) \psi_{n\mathbf{k}}(\mathbf{r}') = \epsilon_{n\mathbf{k}} \psi_{n\mathbf{k}}(\mathbf{r}), \quad (1)$$

where v_{ext} stands for the sum of all nuclear or ionic potentials, V_{H} is the Hartree potential, $\psi_{n\mathbf{k}}(\mathbf{r})$ are the QP orbitals (Dyson orbitals), and $\epsilon_{n\mathbf{k}}$ are the QP energies. In the following sections we refer to $\epsilon_{n\mathbf{k}}$ as the single-particle spectrum.

In practice Eq. (1) is solved using several approximations. The GW technique approximates the self-energy Σ by a dynamically screened exchange-like potential.¹⁹ A large variety

of GW implementations exist, in which quite different levels of approximation are used. Reviews of the GW method can be found in Refs. 20–22. In this study we use the projector Augmented wave (PAW)²³ implementation in the Vienna *ab initio* simulation package (VASP),²⁴ in which the screening is treated fully frequency dependent.

The calculation of the dielectric functions proceeds in a number of steps. First, the self-consistent DFT eigenvalues and KS orbitals are used to construct the DFT Green's function G_0 and dynamically screened interaction W_0 . Subsequently, the QP equation is solved iteratively, adopting certain simplifications. In the simplest approximation, G_0W_0 , the screening in W and the orbitals entering the Green's function are kept fixed at the DFT level. The QP energies are then calculated using first-order perturbation theory.

However, improved single-particle band gaps can be obtained by updating the QP energies in G until self-consistency is reached for the QP energies (so-called GW_0). This typically results in single-particle band gaps within 5%–10% of the experimental value at still moderate computational costs.²⁵ The spectrum is typically converged in four iterations.

Finally the two-particle excitation spectrum is calculated and the dielectric function is constructed. Also here various levels of approximation are possible. The simplest is just to calculate the dielectric function in the independent particle random phase approximation (RPA) from the KS orbitals and eigenvalues. A scissors operator correction can be applied to have the gap coincide with the GW QP gap. We followed this approach in Ref. 15 where we used pseudopotential G_0W_0 results for the scissors correction. This procedure amounts to a neglect of the electron-hole interaction and a neglect of the effect of the GW approximation on other features of the band structures, e.g., the bandwidths. The latter can be incorporated in an RPA calculation starting directly from the GW band structure (denoted by G_0W_0 -RPA or GW_0 -RPA). It yields results that are slightly improved, but often quite similar to those obtained with the scissors-RPA procedure.

For materials with a large band gap, the screening is weak and the electron-hole interactions can be sizable. Such interactions are included in the BSE, usually at the level of electron-hole exchange and electrostatic interactions.^{22,26} In this route (G_0W_0 -BSE or GW_0 -BSE) the results of the GW calculation are used to construct the single-particle spectrum and the statically screened electron-hole interaction [$W(\mathbf{x}, \mathbf{x}'; \omega = 0)$]. The effective two-particle Hamiltonian associated with the BSE reads

$$\begin{aligned} H_{v\mathbf{c}\mathbf{k}, v'\mathbf{c}'\mathbf{k}'} = & (\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}}) \delta_{vv'} \delta_{cc'} \delta_{\mathbf{k}\mathbf{k}'} \\ & + 2 \iint d^3x d^3x' \bar{v}_{c\mathbf{k}}^*(\mathbf{x}) \psi_{v\mathbf{k}}(\mathbf{x}) \\ & \times \bar{v}(\mathbf{x} - \mathbf{x}') \psi_{c'\mathbf{k}'}(\mathbf{x}') \psi_{v'\mathbf{k}'}^*(\mathbf{x}') \\ & - \iint d^3x d^3x' \psi_{c\mathbf{k}}^*(\mathbf{x}) \psi_{v\mathbf{k}}(\mathbf{x}) \\ & \times W(\mathbf{x}, \mathbf{x}'; \omega = 0) \psi_{c'\mathbf{k}'}(\mathbf{x}') \psi_{v'\mathbf{k}'}^*(\mathbf{x}'), \end{aligned} \quad (2)$$

where $\bar{v}$ is the bare Coulomb kernel ($1/|\mathbf{x} - \mathbf{x}'|$).²²

Common to most BSE calculations,²⁷ the polarization is expanded in products of single-particle valence (v) and

conduction (c) band states, where we use products of DFT orbitals. The single-particle energies ($\epsilon_{v\mathbf{k}}, \epsilon_{c\mathbf{k}}$) are the GW QP energies [cf. Eq. (1)]. All valence (except for semi-core) and a limited number, $n_{c,\max}$, of conduction band states are used in the diagonalization. In terms of the eigenvectors $A_{\lambda}^{cv\mathbf{k}}$ and the eigenvalues E_{λ} the dielectric function is obtained as

$$\epsilon(\hat{\mathbf{q}}, \omega) = 1 - \lim_{\mathbf{q} \rightarrow 0} v_0(\mathbf{q}) \frac{1}{\Omega} \int d^3k \sum_{\lambda} \frac{|\sum_{vc} \langle v\mathbf{k} | e^{-i\mathbf{q}\cdot\mathbf{r}} | c\mathbf{k} \rangle A_{\lambda}^{cv\mathbf{k}}|^2}{\omega - E_{\lambda} + i\eta}, \quad (3)$$

where v_0 is the $\mathbf{q} \rightarrow 0$ term of the Coulomb potential.²² Some details of the implementation in VASP can be found in Refs. 28 and 29.

Our starting point for a GW (BSE) calculation is a DFT calculation at the local density approximation (LDA) level. For NaH we additionally check the effect of starting from a generalized gradient approximation (GGA).

Calculations are carried out using the primitive cell. A regular mesh containing Γ is used for the Brillouin zone integration. For NaH we use effectively a $16 \times 16 \times 16$ $\mathbf{k}$ -point mesh,³⁰ and for NaAlH₄ and Na₃AlH₆ we use $6 \times 6 \times 6$ and $6 \times 6 \times 4$ meshes, respectively. The number of conduction band states $n_{c,\max}$ included in the BSE basis is 4, 4, and 12 per formula unit, respectively. This is sufficient to clearly resolve the peak structure of the imaginary part of the dielectric function.

All calculations are carried out with VASP.^{24,31–34} Computational parameters, such as cutoff energies³⁵ and the number of conduction bands included,³⁶ are converged for NaH to an accuracy of 0.1 eV in the GW band gap. These parameters are then also used for NaAlH₄ and Na₃AlH₆. PAW data sets adapted to the large energy range needed for GW calculations were employed. For Na and Al PAW data sets with two reference energies for s , two for p , and two for d are used (six total). For these elements the local pseudopotential is an f -channel pseudopotential. The H PAW data set contains five reference energies (two s , two p , and one d). The reference energies span a range of ~ 4 (Na) to ~ 8 Ryd (H).

NaH crystallizes in the rock salt structure. We use a lattice parameter $a = 4.91$ Å, which has also been adopted in Ref. 11. This lattice parameter is within one percent of the experimental literature values of 4.880 Å (Ref. 37) and 4.89 Å.³⁸ For NaAlH₄ we use the structure from Ref. 15, where the atomic positions have been optimized at the GGA-PW91 level.³⁹ This structure is almost identical to the experimental one of Ref. 40. For Na₃AlH₆ we use the experimental structure from Ref. 41.

III. EXPERIMENTAL RESULTS AND OPTICAL ANALYSIS

Polycrystalline thin NaH films (200 nm) are prepared in an ultrahigh-vacuum rf magnetron sputtering system (base pressure 10^{-7} Pa) at room temperature on $20 \times 10 \times 1.5$ mm³ quartz (Herasil) substrates. NaH is sputtered reactively from a 2" Na metal target under Ar + H₂ flow [flow(Ar) = flow(H₂) = 30 sccm min, total deposition pressure 0.7 Pa]. The thickness is controlled by a quartz crystal monitor (deposition rate $\simeq 0.1$ Å/s)

FIG. 1. (Color online) Bottom panel: OJL fit (dashed lines) of experimental reflectance R and transmittance T data (circles) of NaH film. Top panel: NaH dielectric function obtained from OJL fit.

The optical reflectance R and transmittance T measurements of the NaH thin films are performed in a Perkin–Elmer λ 900 diffraction grating spectrometer with an energy range from 0.495 to 6.5 eV ($\lambda = 2500$ –190 nm).⁴² Dielectric constants of the NaH layer are extracted from the reflectance and transmittance measurements of the NaH/quartz stack using the SCOUT software.⁴³ The dielectric constants of quartz are determined independently by the reflectance and transmittance measurements of the bare substrate. The reflectance and transmittance of the NaH/quartz stack are calculated using a transfer matrix method that considers the Fresnel reflectance and transmittance coefficients at each interface and the absorption in each layer.⁴⁴ The modeled thickness of the NaH layer is 201 nm, in agreement with the quartz crystal monitor thickness determination.

The NaH optical band gap edge is modeled by the O’Leary–Johnson–Lim (OJL) model.⁴⁵ This model provides the best fit to the experimental data (Fig. 1). The OJL model assumes interband transitions from the valence band to the conduction band and parabolic bands with tails exponentially decaying into the band gap. The model includes the band gap E_g and the tail exponent γ as fit parameters. The imaginary part of the dielectric function is assumed to be proportional to the joint density of states of the valence and conduction bands. Without modification, the original OJL expression for the imaginary part of the dielectric function would increase to infinity with increasing energy. This unphysical behavior would also prevent the construction of the real part of the dielectric function. Therefore, a decay function has been added to the original OJL expression to force the imaginary part to go to zero for high frequencies. The OJL term is multiplied with $\exp(-\sqrt{(E - E_g)/d})$, with d being a decay parameter. From the fit to the experimental reflectance and transmittance, we find the parameters $E_g = 5.82$ eV, $\gamma = 0.12$ eV, and $d = 0.25$ eV. The dielectric function based upon the OJL model is also shown in Fig. 1.

As an alternative we have also used the Tauc–Lorentz model to fit the data. The position of the peak in ϵ_2 (and the node in ϵ_1) is then hardly affected, but its intensity is about a

factor of 2 larger. In this model the reflection and transmission spectrum are slightly less well reproduced. We conclude that the peak position at 6.08 eV is robust, but its intensity is model dependent.

IV. COMPUTATIONAL RESULTS AND DISCUSSION

A. NaH

The calculated single-particle gaps of NaH are listed in Table I. The single particle gaps are defined as $E_g = \min_{\mathbf{k}, \mathbf{k}'} (\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}'})$. As expected G_0W_0 gives a considerable widening of the gap as compared to DFT-LDA. GW_0 results in an even larger gap, consistent with the general trend observed in Ref. 25 for a large set of semiconductors. The LDA and G_0W_0 gaps of NaH presented here are slightly larger (~ 0.1 – 0.2 eV) than those in the G_0W_0 calculation of Lebègue *et al.*,¹¹ who also used a PAW approach. Although there are slight differences in the computational approach (see Ref. 24) we think it is more likely to attribute the gap differences to different PAW data sets, as small differences already occur at the LDA level.

Comparing to our previous G_0W_0 study, we find somewhat larger differences. In those pseudopotential calculations the contribution of the core electrons was accounted for by a simple DFT-based estimate,¹⁵ yielding a gap of 5.50 eV, about 0.4 eV below our current value. We attribute this difference to an improved treatment of the core-valence exchange, which in the present study is treated at the Hartree-Fock level.^{24,46} The $2p$ core states of Na being rather shallow makes this a likely explanation.

The calculated optical gaps of NaH (calculated starting from the GW_0 single-particle spectrum) are also listed in Table I. At the RPA level the optical gap corresponds to the minimum direct single-particle gap, $E_{\text{opt}}^{\text{RPA}} = \min_{\mathbf{k}} (\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}})$, whereas at the BSE level the optical gap is given by the minimum excitation energy, $E_{\text{opt}}^{\text{BSE}} = \min_{\lambda} E_{\lambda}$ [cf. Eqs. (2) and (3)]. The difference between the two is due to excitonic effects and may be called the exciton binding energy, which for NaH is relatively large, i.e., 1.08 eV.

We also check the effect of starting from a DFT-GGA (PBE, Ref. 47) instead of a DFT-LDA calculation (keeping the same PAW data sets, i.e., unscreened at the LDA level). The GGA single-particle gap for NaH is ~ 0.3 eV larger than the LDA gap (see Table I). This difference is halved at the G_0W_0 and GW_0 levels. It remains in the optical gap at the GW_0 -RPA level, but it disappears at the GW_0 -BSE level, suggesting that at the highest level of approximation the DFT starting point is less important.

TABLE I. Calculated single-particle band gaps E_g (eV) and optical gaps E_{opt} (eV). The usual starting point for GW is a DFT-LDA calculation; “(GGA)” indicates that GGA is used instead of LDA.

	E_g^{DFT}	$E_g^{G_0W_0}$	$E_g^{GW_0}$	$E_{\text{opt}}^{GW_0/\text{RPA}}$	$E_{\text{opt}}^{GW_0/\text{BSE}}$
NaH	3.33	5.86	6.40	7.33	6.25
Na ₃ AlH ₆	2.33	4.86	5.33	5.32	4.83
NaAlH ₄	4.17	6.88	7.37	7.38	6.68
NaH (GGA)	3.66	6.01	6.55	7.47	6.25

FIG. 2. (Color online) Dielectric function of NaH; $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are the real and the imaginary part, respectively. The top and bottom two figures result from using the GW_0 and G_0W_0 spectra. The BSE and RPA results are given by the (black) solid lines and the (blue) dashed lines. The experimental dielectric function from Fig. 1 is indicated by the (red) dotted lines. Vertical arrows indicate the single-particle GW_0 gaps.

Figure 2 shows the dielectric function of NaH as calculated with RPA and BSE, with the G_0W_0 or GW_0 spectra as input. Going from G_0W_0 to GW_0 blue-shifts the dielectric function by ~ 0.5 eV, for both RPA and BSE. This shift is already apparent in the single-particle gap, compare $E_g^{G_0W_0}$ to $E_g^{GW_0}$ in Table I. Going from RPA to BSE the effects seem to be more dramatic. The optical gap red-shifts by the exciton binding energy (1.08 eV). As the effects on the dielectric function of going from G_0W_0 to GW_0 and going from RPA to BSE work in opposite directions, there is a partial cancellation of errors in the optical gap, comparing the simplest (G_0W_0 -RPA) approach to the most advanced (GW_0 -BSE) approach. This is even more so if one compares to pseudopotential G_0W_0 -RPA, where the effects of core electrons are accounted for by a simple estimate giving a smaller single particle gap (see the preceding discussion). Due to this fortuitous cancellation of errors the optical gap found in Ref. 15 was 6.37 eV, close to the present GW_0 -BSE value of 6.25 eV. The shape of the spectrum is, however, affected very much in going from RPA to BSE, or, in other words, by including excitonic effects. The response seems to narrow into a single resonance, and the main oscillator strength is transferred to just above the onset of $\epsilon_2(\omega)$. It is tempting to describe the response in the BSE spectrum by a single Lorentz oscillator and assign it to an exciton.

If we compare the calculated to the experimental dielectric functions (Fig. 2), it is clear that the position of the experimental resonance (the peak in ϵ_2 and the node in ϵ_1) is best described by the GW_0 -BSE results. The experimental peak position is at 6.08 eV, whereas the GW_0 -BSE peak is at 6.25 eV (corresponding to the optical gap $E_{\text{opt}}^{GW_0/\text{BSE}}$, see Table I). The optical G_0W_0 -BSE gap is too small, whereas the RPA gap is too large. There is a considerable difference in height of the

resonance peak between the experimental and the GW_0 -BSE spectra. As discussed in Sec. III the experimentally extracted height is model dependent. On the other hand overestimation of the intensities in GW -BSE-type calculations is also known to occur more often.

In conclusion, the position of the experimental resonance is quite accurately reproduced at the GW_0 -BSE level, and excitonic effects cannot be ignored in modeling the dielectric function. NaH is characterized by a relatively simple bonding between Na^+ and H^- ions.^{11,15} Its strong exciton peak and the considerable exciton binding energy are reminiscent of the ones observed in alkali halides.⁴⁸

B. Alanates

Before discussing the optical response function of NaAlH_4 and Na_3AlH_6 , first we briefly discuss the single-particle gaps, which are listed in Table I. For NaAlH_4 at the G_0W_0 level we obtain a gap that is 0.5 eV higher than the one in Ref. 15. As the latter calculations were based upon pseudopotentials, we ascribe the difference, as in the case of NaH, to an improved treatment of the (semi)core electrons in the present calculation. Using pseudopotentials Peles *et al.*¹⁴ obtained a single-particle gap that is close to the present one. That is probably somewhat fortuitous, however, as a GGA calculation was chosen as a starting point, whereas we choose LDA to start from, and the difference between the LDA and GGA gaps is already 0.5 eV.¹⁵ For Na_3AlH_6 at the G_0W_0 level we obtain a gap that is 1.0 eV higher than that in our previous study. A difference of 0.4 eV occurs already at the LDA level, because we use a slightly different input crystal structure here. As before, the remainder can be attributed to an improved treatment of the (semi)core electrons. Incorporating (partial) self-consistency ($G_0W_0 \rightarrow GW_0$) increases the single-particle gap in NaAlH_4 and Na_3AlH_6 by ~ 0.5 eV, as in the case of NaH.

The dielectric functions of NaAlH_4 and Na_3AlH_6 are plotted in Fig. 3. As for NaH, the functions using the GW_0 single-particle spectra as a starting point are blue-shifted by ~ 0.5 eV with respect to the ones based upon G_0W_0 . The difference between the RPA and BSE responses, caused by excitonic effects, is again sizable. The RPA and BSE optical gaps differ by 0.77 eV in NaAlH_4 and by 0.49 eV in Na_3AlH_6 , giving a corresponding red shift in going from RPA to BSE. Associating these numbers with an exciton binding energy, one observes that they are smaller than those for NaH, but again in a range that is typical for large band gap ionic materials.⁴⁸ Going from the simplest (G_0W_0 -RPA) to the most advanced (GW_0 -BSE) approach, the blue and red shifts discussed previously partially cancel. Comparing the NaAlH_4 GW_0 -BSE optical gap (6.68 eV) to a pseudopotential G_0W_0 -RPA value (6.50 eV)¹⁵ one again finds that the two are fortuitously close due to a cancellation of errors.

The most dramatic effect of including excitonic effects (RPA $\rightarrow$ BSE) is a renormalization of oscillator strength. In contrast to the RPA ϵ_2 (which is based upon independent electron-hole response), the BSE ϵ_2 of NaAlH_4 and Na_3AlH_6 have large peaks just above their onsets, which is typical of absorption by excitons. The BSE dielectric function of NaAlH_4 , and even more so that of Na_3AlH_6 , cannot be described by a single Lorentz oscillator, however, in contrast to the BSE dielectric function of NaH (cf. Fig. 2).

FIG. 3. (Color online) Directionally averaged real [$\epsilon_1(\omega)$] and imaginary [$\epsilon_2(\omega)$] parts of the calculated dielectric functions of Na_3AlH_6 (top panels) and NaAlH_4 (bottom panels). Dashed lines, G_0W_0 dielectric functions; solid lines, GW_0 dielectric functions; black (thick) lines, BSE; blue (thin) lines, RPA. Vertical arrows indicate the single-particle GW_0 gaps.

V. SUMMARY AND CONCLUSIONS

Dielectric functions are calculated for NaH, NaAlH_4 , and Na_3AlH_6 . These hydride materials are the protagonists in the archetypical sodium alanate hydrogen storage system. To benchmark the calculations, the optical response (reflectance and transmittance) of a thin film of NaH is measured. From these measurements we extract the dielectric function. It can be characterized by an oscillator with a resonance energy of 6.08 eV.

We study the effects of systematic improvements of the theoretical description. Starting from a single-particle spectrum at the G_0W_0 level, the simplest computational scheme is based upon the response of independent particles (RPA). Improvements include partial self-consistency in the single-particle spectrum (GW_0) and account for electron-hole interactions (excitons) via the Bethe-Salpeter equation (BSE). Going from G_0W_0 to GW_0 gives a blue shift in the optical gap of ~ 0.5 eV, whereas going from RPA to BSE gives a red shift of 0.4–1.1 eV. These shifts partially cancel at the highest (GW_0 -BSE) level of approximation. Moreover, the relative order of the band gaps in NaH, NaAlH_4 , and Na_3AlH_6 , both single-particle and optical, is the same at all levels of approximation.

Including exciton effects markedly alters the distribution of oscillator strengths. The dielectric response as a function of frequency is narrowed and transitions just above the absorption onset become very strong. Indeed the response of NaH seems to narrow into a single resonance, whereas that of NaAlH_4 and Na_3AlH_6 remains more complicated. The resonance in NaH peaks at 6.25 eV, which is close to the experimental value. In conclusion, GW_0 -BSE calculations, requiring only a few iterations on the eigenvalues in G , are an accurate yet

cost-effective means of calculating optical spectra for complex hydrides.

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