1. Introduction.

In Drude model mobility is given by:

$$\mu = \frac{q\tau}{m^*} \quad (1),$$

where q is the charge, τ is the relaxation (scattering) time of a charge carrier and m^* is the effective mass of the carrier. Under an external electric field, which is treated classically, the effective mass of a charge carrier is defined as:

$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2}\frac{\partial^2 E_n(\vec{k})}{\partial k_i k_j}, \quad i,j = x,y,z \quad (2),$$

where indices i and j denote reciprocal components, and $E_n(k)$ is the dispersion relation for the n-th band. For covalently bonded group III-IV semiconductors, the dispersion relation at the band minimum (or maximum) can be approximated by a parabola:

$$E_n(\vec{k}) = \alpha_1 k_x^2 + \alpha_2 k_y^2 + \alpha_3 k_z^2 \quad (3).$$

Thus, components of the effective mass tensor are just the inverse of the coefficients in front of the quadratic term:

$$m_{xx}^* = \frac{\hbar}{2\alpha_1}; \ m_{yy}^* = \frac{\hbar}{2\alpha_2}; \ m_{zz}^* = \frac{\hbar}{2\alpha_3} \quad (4).$$

Effective masses evaluated using this methodology are in good agreement with experimental obtained values for group III-IV semiconductors [1]. However, in the case of organic semiconductors, it is not always possible to fit the band to a quadratic polynomial. In this case, derivatives can be evaluated numerically, using finite difference method. The explicit form of the right-side symmetric tensor in (2) is:

$$\frac{d^2 E}{dk^2} = \begin{pmatrix} \frac{d^2 E}{dk_x^2} & \frac{d^2 E}{dk_x dk_y} & \frac{d^2 E}{dk_x dk_z} \\ \frac{d^2 E}{dk_x dk_y} & \frac{d^2 E}{dk_y^2} & \frac{d^2 E}{dk_y dk_z} \\ \frac{d^2 E}{dk_x dk_z} & \frac{d^2 E}{dk_y dk_z} & \frac{d^2 E}{dk_z^2} \end{pmatrix} \quad (5),$$

where second and mixed derivatives are evaluated on five-point stencil (h is step size), with error of the order of $O(h^4)$ [2]:

$$\frac{\partial^2 f}{\partial x^2} \approx \frac{1}{12h^2}\begin{pmatrix} -(f_{-2} + f_2)+ \\ 16(f_{-1} + f_1)+ \\ -30(f) \end{pmatrix} \quad (6),$$

$$\frac{\partial^2 f}{\partial x \partial y} \approx \frac{1}{600h^2} \begin{pmatrix} -63(f_{1,-2} + f_{2,-1} + f_{-2,1} + f_{-1,2}) + \\ 63(f_{-1,-2} + f_{-2,-1} + f_{1,2} + f_{2,1}) + \\ 44(f_{2,-2} + f_{-2,2} - f_{-2,-2} - f_{2,2}) + \\ 74(f_{-1,-1} + f_{1,1} - f_{1,-1} - f_{-1,1}) \end{pmatrix} \quad (7).$$

Following equations (2) and (5-7), the effective mass components are the inverse of the eigenvalues of (5) and the principal directions correspond to the eigenvectors.

2. Computational methodology.

For calculations with the pure functional (PBE [3,4]) PAW method [5,6] as implemented in VASP was used [7-10]. Plane wave energy cut-offs of 500 eV for III-IV binary compounds and 450 eV for organic crystals were employed. The Brillouin zone (BZ) integration was performed on a Γ-centered k-point mesh using Gaussian smearing with the width of 0.02 eV. For III-IV binary compounds, the electronic density was integrated over 504 irreducible k-points on a uniform 10x10x10 mesh. For pentacene crystals mesh of 8x6x4 was chosen with 100 irreducible k-points. For rubrene crystal, mesh of 6x6x6 with 112 irreducible k-points was chosen. Symmetry constraints were turned off in all calculations with VASP. For calculations with hybrid functional (PBE0 [11]) localized atomic orbitals as implemented in CRYSTAL09 was used [12]. DFT integration grid was set to XXLGRID in the case of binary compounds and XLGRID in the case of organic crystals. For the III-IV binary compounds pseudopotentials generated by Dovesi *et al.* were employed [13]. For organic crystals, the 6-31G basis set was used. Similar k-mesh for BZ as in case of PBE functional was employed. Geometry relaxations were performed by constraining the unit cell shape and volume from experimental data.

3. Results for binary crystals.

In order to better understand how well the results from parabolic fitting [14] can be reproduced with the finite difference method and how they compare to experiment, we first start with discussion of inorganic systems. Two binary compounds were chosen: (i) GaAs – as a benchmark and (ii) InP – whose heavy hole effective mass (0.531 m_e) is comparable to the smallest effective masses reported for organic crystals. The following lattice constants were used: 5.648Å for GaAs and 5.869Å for InP.

GaAs and InP have degenerate energy at Γ-point, resulting in light and heavy hole effective masses. The effective mass of the heavy hole (HH) was computed from the valence band (VB) curvature, for light hole (LH) the VB-2 curvature was used. In the case of GaAs, PBE functional predicts m^* of light hole (LH) similar to parabola-fitted value with steps: 0.005 and 0.01 (1/Bohr). The

experimental value is achieved somewhere in-between 0.04 and 0.05 (1/Bohr) steps. For the heavy hole (HH), m^* is closer to the experimental values when compared to the results from previous calculations. Already at step 0.005 (1/Bohr), the difference between our calculation and experiment is only 1.7%; the step value of 0.07 (1/Bohr) gives the experimental value. For the electron, the situation is very similar to the LH: the experimental result is reproduced at a step value of 0.07 (1/Bohr). Results obtained using the PBE0 functional, as implemented in CRYSTAL code, completely failed to reproduce small effective masses for light hole and electron. The heavy holes values are comparable with those obtained with HSE functional, and thereby the experimental values were never achieved. A step larger than 0.1 (1/Bohr) should be employed to get m^* closer to experiment.

Very similar trends are obtained for the InP crystal. For PBE functional, previous calculated m^* value for LH is reproduced on step of 0.04 (1/Bohr). LH m^* converges to experimental value as the step-size increases. Predicted value for HH is larger than that derived from the fit but lower than what is obtained from the experiment. For the electron, the finite difference method agrees with experiment at step of 0.05 (1/Bohr).

Table 1. Effective light hole (LH), heavy hole (HH) and electron (El) masses calculated at the Γ-point in the units of the mass of electron at rest (m_e). Calculated values correspond to parabola fitted data by Kresse *et al.* [14]. For PBE0 column, HSE values are listed as calculated. Experimental values are those recommended by Vurgaftman *et al.* [1].

	GaAs						InP					
	PBE			PBE0			PBE			PBE0		
Step, 1/Bohr	LH	HH	El	LH	HH	El	LH	HH	El	LH	HH	El
0.005	0.036	0.344	0.036	0.154	0.322	0.377	0.058	0.439	0.058	0.136	0.405	0.182
0.010	0.036	0.344	0.036	0.152	0.317	0.374	0.058	0.438	0.058	0.136	0.406	0.182
0.015	0.037	0.344	0.038	0.151	0.316	0.381	0.059	0.438	0.059	0.136	0.405	0.181
0.020	0.039	0.344	0.040	0.151	0.315	0.395	0.060	0.438	0.061	0.135	0.403	0.159
0.025	0.042	0.344	0.042	0.150	0.315	0.416	0.062	0.438	0.063	0.136	0.403	0.152
0.030	0.045	0.344	0.045	0.150	0.315	0.443	0.065	0.438	0.066	0.136	0.404	0.151
0.035	0.048	0.344	0.048	0.150	0.315	0.476	0.068	0.439	0.069	0.136	0.404	0.203
0.040	0.051	0.345	0.050	0.151	0.315	0.514	0.071	0.439	0.072	0.136	0.403	0.263
0.050	0.083	0.346	0.055	0.151	0.316	0.604	0.078	0.440	0.079	0.137	0.404	0.400
0.060	0.088	0.348	0.061	0.152	0.317	0.717	0.086	0.442	0.086	0.139	0.405	0.557
0.070	0.094	0.351	0.067	0.153	0.319	0.857	0.094	0.444	0.092	0.141	0.407	0.726
0.080	0.085	0.355	0.088	0.155	0.322	1.030	0.102	0.447	0.099	0.144	0.409	0.897
0.090	0.085	0.359	0.112	0.157	0.326	1.249	0.109	0.451	0.106	0.147	0.412	1.062
0.100	0.091	0.364	0.138	0.159	0.330	1.532	0.115	0.455	0.114	0.147	0.415	1.211
Calc.	0.036	0.320	0.030	0.085	0.314	0.067	0.073	0.435	0.054	0.117	0.479	0.085
Expt.	0.073	0.350	0.067				0.121	0.531	0.080			

4. Results for organic crystals.

In order to further test our code, we have chosen two representative organic crystals that showed highest mobilities so far measured in single crystal FETs: pentacene and rubrene. For the highly-purified vacuum-deposited single crystal of pentacene mobility of 35 (cm^2/Vs) was reported [15]. Rubrene is a p-type semiconductor with the highest carrier mobility to the date (40 cm^2/Vs) [16].

We evaluated effective masses for the pentacene crystal at different temperatures. At 120K (low temperature, LT) unit cell parameters are: a=6.292(2), b=7.6901(13), c=14.4103(16) Å, and α=76.861(13), β=88.16(2), γ=84.36(2)° (CSD code: PENCEN06 [17]); at room temperature (RT) unit cell parameters are: a=6.2873(9), b=7.8058(9), c=14.5799(11) Å, and α=76.461(8), β=87.629(10), γ=84.707(10)° (CSD code: PENCEN07 [17]). The polymorph of rubrene crystal obtained at RT with unit cell parameters: a=26.860(10), b=7.193(3), c=14.433(5)Å (CSD code: QQQCIG11 [18]) was chosen. This polymorph was used in several previous experimental studies [19,20].

Effective masses for pentacene crystals were previously calculated using both pure (PBE) [21] and hybrid (B3LYP [22,23]) [24] GGA functionals. In both cases, authors calculated effective masses using finite difference method on three-point stencil. In the case of the PBE functional, our calculations give the smallest effective mass in the range of 1.762–1.862 m_e for LT, and 1.984–2.240 m_e for RT (Table 2). These values are in good agreement with previously calculated results [21]. Prior calculations with B3LYP functional were made for the exact same crystal structures [24]. If it is assumed that the increase of Hartree-Fock exchange percentage by 5% (from B3LYP to PBE0) does not bring significant changes in m^* values, it is possible to assess the effect of larger grid in the finite difference method. The smallest mass (m_1) obtained from crystal at 120K is slightly smaller for all steps than previously calculated. Similarly, m_2 is smaller for all steps except 0.09 and 0.10 (1/Bohr). Conversely, m_3 values vary around the previously computed value depending on the step-size. The smallest mass (m_1) obtained from crystal at RT is slightly larger for all steps except 0.08 and 0.09 (1/Bohr), than previously calculated. Conversely, m_2 is smaller for all steps except 0.08, 0.09 and 0.10 (1/Bohr). Lastly, m_3 is larger for all steps compared to the previously computed value. The effect of geometry relaxation on effective mass can be realized by comparing data from Table S2. For crystal at LT, the smallest effective mass increases for relaxed structure by 2–2.5% compared to the X-ray geometry. The opposite effect is seen for the crystal at RT, m^* decreases from X-ray to relaxed geometry by 0.6–1.4%.

The dependence of m^* with step size for rubrene crystal is listed in Table S1.

Table 2. For pentacene, effective masses for holes were calculated at M-point (0.375, 0.5, 0.075) in the units of the mass of electron at rest (m_e). For PBE column, calculated values correspond to a different pentacene polymorph reported in crystalline films although with similar unit cell parameters [21]. For PBE0 column, calculated values correspond to data from B3LYP calculations [24]. In both cases finite difference method on three-point stencil was employed. Only the smallest effective mass is listed as experimental value [25].

| | Pentacene at 120K (PENCEN06) | | | | | | Pentacene at RT (PENCEN07) | | | | | |
| | PBE | | | PBE0 | | | PBE | | | PBE0 | | |
Step, 1/Bohr	m_1	m_2	m_3	m_1	m_2	m_3	m_1	m_2	m_3	m_1	m_2	m_3
0.005	1.862	5.211	10.052	1.477	5.723	9.035	2.240	10.522	17.215	1.690	6.537	12.389
0.010	1.762	6.223	10.406	1.453	5.756	9.173	2.022	7.667	13.724	1.681	6.542	12.383
0.015	1.777	6.095	9.660	1.458	5.768	9.203	2.013	6.780	12.274	1.668	6.551	12.383
0.020	1.770	5.925	10.339	1.455	5.785	9.229	2.036	6.940	13.294	1.671	6.565	12.398
0.025	1.766	5.901	10.322	1.452	5.791	9.227	2.004	6.874	13.236	1.672	6.572	12.400
0.030	1.787	5.897	10.307	1.455	5.801	9.224	2.013	6.966	13.363	1.668	6.582	12.400
0.035	1.785	5.939	10.347	1.454	5.816	9.180	2.006	7.046	13.386	1.670	6.597	12.347
0.040	1.782	6.017	10.251	1.452	5.839	9.174	2.009	7.127	13.285	1.667	6.622	12.352
0.050	1.781	6.035	10.249	1.452	5.915	9.159	2.008	7.263	13.013	1.670	6.700	12.354
0.060	1.781	6.124	10.209	1.453	6.049	9.135	2.010	7.378	12.930	1.669	6.857	12.357
0.070	1.782	6.308	10.115	1.452	6.270	9.086	2.007	7.597	12.906	1.667	7.120	12.347
0.080	1.773	6.603	10.303	1.443	6.616	9.399	1.985	7.996	13.713	1.646	7.532	13.523
0.090	1.765	7.085	10.331	1.432	7.137	9.853	1.984	8.591	13.459	1.640	8.151	13.944
0.100	1.775	7.812	9.567	1.455	7.839	8.659	2.000	9.518	12.058	1.674	9.027	11.470
Calc.				1.50	6.72	9.15	1.84	7.45	44.93	1.65	7.34	10.64
Expt.							2–3					

5. Discussion and conclusions.

We have implemented and tested the code for the effective mass calculation using finite difference method on a five-point stencil. We obtained excellent agreement with previous calculations performed for III-IV semiconductors using PBE functional in VASP package. However, we have showed that the current implementation of the CRYSTAL program fails to reproduce small values of the effective masses for GaAs and InP crystals. The reasons for that may be due to the inaccuracy of the energy value for a chosen k-point. We also calculated effective masses for two organic crystals at different temperatures: pentacene and rubrene. Our results are in good agreement with data previously reported in the literature. We showed that dependence of the effective mass value with step size proved to be somewhat unpredictable, and that the effective mass values may increase or decrease for a relaxed structure. The only trend that holds is the decrease of effective mass values (and thus increase of the intersite electronic coupling) with the increase percentage of Hartree-Fock exchange incorporated in the employed functional (going from PBE [0% HF] to PBE0 [25% HF]). This trend was recently examined. Thus, we suggest computing effective masses for a range of different differentiation steps in order to estimate deviation. Also, we found that PBE0 results are in good agreement with those obtained with B3LYP functional (for organic crystals) suggesting that the increase of HF exchange by 5% (from B3LYP to PBE0) did not bring any significant changes to effective hole masses.

As a future planes, a version of the code for Quantum Espresso code [26] is intended. Also, we plan to reevaluate the effective masses using freshly optimized pob-TZVP basis sets in CRYSTAL [27].

Appendix.

The newest version of the code is freely available at: https://github.com/alexandr-fonari/EMC.

References:

[1]   Vurgaftman, I.; Meyer, J. R.; Ram-Mohan, L. R. *J. Appl. Phys.* **2001**, *89*, 5815.

[2]   Abramowitz, M.; Stegun, I. *Handbook of Mathematical Functions: with Formulas, Graphs, and Mathematical Tables*; Dover, 1972.

[3]   Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

[4]   Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396.

[5]   Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.

[6]   Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.

[7]   Kresse, G.; Furthmüller, J. *Comput. Mat. Sci.* **1996**, *6*, 15.

[8]   Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.

[9]   Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558.

[10]   Kresse, G.; Hafner, J. *Phys. Rev. B* **1994**, *49*, 14251.

[11]   Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

[12]   Dovesi, R.; Orlando, R.; Civalleri, B.; Roetti, C.; Saunders, V. R.; Zicovich-Wilson, C. M. *Z. Kristallogr.* **2005**, *220*, 571.

[13]   Causà, M.; Dovesi, R.; Roetti, C. *Phys. Rev. B: Condens. Matter* **1991**, *43*, 11937.

[14]   Kim, Y.-S.; Marsman, M.; Kresse, G.; Tran, F.; Blaha, P. *Phys. Rev. B: Condens. Matter* **2010**, *82*, 205212.

[15]   Jurchescu, O. D.; Baas, J.; Palstra, T. T. M. *Appl. Phys. Lett.* **2004**, *84*, 3061.

[16]   Tatsuo, H.; Jun, T. *Sci. Technol. Adv. Mater.* **2009**, *10*, 024314.

[17]   Siegrist, T.; Besnard, C.; Haas, S.; Schiltz, M.; Pattison, P.; Chernyshov, D.; Batlogg, B.; Kloc, C. *Adv. Mater.* **2007**, *19*, 2079.

[18]   Jurchescu, O. D.; Meetsma, A.; Palstra, T. T. M. *Acta Crystallogr. Sect. B: Struct. Sci.* **2006**, *62*, 330.

[19]   Menard, E.; Marchenko, A.; Podzorov, V.; Gershenson, M. E.; Fichou, D.; Rogers, J. A. *Adv. Mater.* **2006**, *18*, 1552.

[20]   Li, Z. Q.; Podzorov, V.; Sai, N.; Martin, M. C.; Gershenson, M. E.; Di Ventra, M.; Basov, D. N. *Phys. Rev. Lett.* **2007**, *99*, 016403.

[21]   Yoshida, H.; Sato, N. *Phys. Rev. B: Condens. Matter* **2008**, *77*, 235205.

[22]   Becke, A. D. *Phys. Rev. A: At. Mol. Opt. Phys.* **1988**, *38*, 3098.

[23]   Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785.

[24]   Li, Y.; Coropceanu, V.; Brédas, J.-L. *J. Phys. Chem. Lett.* **2012**, *3*, 3325.

[25]   Hatch, R. C.; Huber, D. L.; Höchst, H. *Phys. Rev. Lett.* **2010**, *104*, 047601.

[26]   Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; Corso, A. D.; Gironcoli, S. d.; Fabris, S.; Fratesi, G.; Gebauer, R.; Gerstmann, U.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-Samos, L.; Marzari, N.; Mauri, F.; Mazzarello, R.; Paolini, S.; Pasquarello, A.; Paulatto, L.; Sbraccia, C.; Scandolo, S.; Sclauzero, G.; Seitsonen, A. P.; Smogunov, A.; Umari, P.; Wentzcovitch, R. M. *J. Phys.: Condens. Matter* **2009**, *21*, 395502.

[27]   Peintinger, M. F.; Oliveira, D. V.; Bredow, T. *J. Comput. Chem.* **2013**, *34*, 451.

Supporting information

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Table S1. For rubrene, effective masses for holes were calculated at Γ-point in the units of the mass of electron at rest (m_e). For PBE column, calculated values correspond to parabola fitted data [1]. For PBE0 column, calculated values correspond to data from B3LYP calculations [2]. In the latter case, finite difference method on three-point stencil was employed. Experimental values are from ref. [1].

| | Rubrene (QQQCIG11) X-ray | | | | | |
| | PBE | | | PBE0 | | |
Step, 1/Bohr	m_1	m_2	m_3	m_1	m_2	m_3
0.005	0.996	2.365	13.383	0.823	2.166	11.925
0.010	0.977	2.502	12.230	0.823	2.166	11.891
0.015	0.980	2.501	12.542	0.823	2.166	11.882
0.020	0.981	2.444	12.250	0.823	2.166	11.882
0.025	0.980	2.456	12.274	0.823	2.166	11.891
0.030	0.980	2.450	11.630	0.820	2.167	11.910
0.035	0.978	2.455	10.787	0.820	2.167	10.989
0.040	0.979	2.462	10.219	0.821	2.167	10.476
0.050	0.978	2.464	10.157	0.821	2.169	10.358
0.060	0.978	2.392	10.569	0.819	2.102	10.841
0.070	0.977	2.209	17.360	0.819	1.935	17.757
0.080	0.975	2.140	33.545	0.819	1.874	34.465
0.090	0.974	2.135	78.091	0.817	1.866	79.405
0.100	0.972	2.161	217.982	0.817	1.891	209.847
Calc.	1.0–1.2	1.9–2.8		0.84	1.95	11.43
Expt.	0.8	1.9				

Table S2. For relaxed geometry of pentacene using PBE0 functional, effective masses for holes were calculated at M-point (0.375, 0.5, 0.075) in the units of the mass of electron at rest (m_e).

Step, 1/Bohr	Relaxed pentacene crystal using PBE0 functional						For comparison, pentacene crystal using PBE0 functional	
	120K			RT			120K	RT
	m_1	m_2	m_3	m_1	m_2	m_3	m_1	m_1
0.005	1.511	4.298	7.940	1.667	4.877	9.118	1.477	1.690
0.010	1.490	4.263	8.146	1.667	4.832	9.398	1.453	1.681
0.015	1.496	4.259	8.192	1.656	4.827	9.465	1.458	1.668
0.020	1.493	4.262	8.226	1.659	4.830	9.496	1.455	1.671
0.025	1.489	4.264	8.234	1.661	4.834	9.512	1.452	1.672
0.030	1.493	4.269	8.246	1.657	4.841	9.527	1.455	1.668
0.035	1.491	4.279	8.222	1.659	4.852	9.499	1.454	1.670
0.040	1.489	4.293	8.237	1.656	4.870	9.517	1.452	1.667
0.050	1.489	4.346	8.261	1.659	4.931	9.545	1.452	1.670
0.060	1.490	4.448	8.271	1.657	5.054	9.565	1.453	1.669
0.070	1.488	4.620	8.241	1.656	5.261	9.539	1.452	1.667
0.080	1.473	4.888	8.717	1.626	5.579	10.625	1.443	1.646
0.090	1.462	5.295	9.008	1.628	6.061	10.441	1.432	1.640
0.100	1.493	5.888	7.618	1.663	6.755	8.731	1.455	1.674

References:

[1]   Li, Z. Q.; Podzorov, V.; Sai, N.; Martin, M. C.; Gershenson, M. E.; Di Ventra, M.; Basov, D. N. *Phys. Rev. Lett.* **2007**, *99*, 016403.
[2]   Li, Y.; Coropceanu, V.; Brédas, J.-L. *J. Phys. Chem. Lett.* **2012**, *3*, 3325.