MedeA Electronics: What the Electrons at the Fermi Sea Can Tell Us

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Electronics gives you access to the so-called low-energy excitations. Under this term, physicists subsume all those electronic properties, which involve electronic states in a narrow energy range around the Fermi energy, usually within a few $k_B T$. Of course, a lot of information can be deduced from the electronic states at the Fermi energy itself as, *e.g.*, the Fermi surface. Yet, including electronic states nearby allows investigating electronic transport.

Specifically, *Electronics* allows you to calculate the electronic energies as a function of the **k**-vector on a regular 3-dimensional (3D) mesh spanning the Brillouin zone. You can then display 3-dimensional isoenergy surfaces of the band structure and compute effective masses and band velocities on a given surface. In particular, for metals *Electronics* yields the Fermi surface. In addition, an estimate of effective electron masses can be made (precise effective masses are obtained via the "Electronic Mass" stage in a Flowchart).

To run *Electronics* jobs, select Electronics from the Tools menu, click the new menu entry Electronics in the *MedeA* main menu and select Run .

The Run interface is similar to what you know from the SCF panel of the VASP interfaces. Select a rather fine mesh of **k**-points, with a Spacing of k-points such as 0.15 Å^{-1} (default 0.3 Å^{-1}), the number of points to be used per VASP task (default Points per task = 25), and select further VASP Settings to set additional VASP parameters. The module will determine a 3-dimensional **k**-point mesh for the Brillouin zone of the current structure (periodic lattice) and run several VASP tasks to yield the electronic energies on the **k**-points of the 3D mesh for later visualization.

In addition, *Electronics* allows calculating electronic transport properties using Boltzmann theory as implemented in the BoltzTraP [1] code. This includes particularly the electronic conductivity, the thermoelectric power, the electronic contribution to the thermal conductivity, and the electronic specific heat. These quantities can be calculated for a set of temperatures and a range of chemical potentials, the latter mimicking the effect of doping within a rigid band scheme. Finally, for semiconductors and insulators, the code allows adjusting the optical band gap to the desired value (this is also known as the scissors operator approach).

To this end, the right part of the Run Electronics interface offers fields to specify the Range of chemical potentials (extending from E_F - 2.0 eV to E_F + 2.0 eV in the example above), the Maximum temperature , the Temperature step , and the optical Band gap of semiconductors and insulators in case this should be adapted. The Energy step field allows you to customize the energy increment for numerical integrations, which can be useful the accuracy of the integration algorithm. Finally, the interface offers a choice between the Histogram method and the linear Tetrahedron method for Brillouin zone integration, the latter of which is recommended.

Care should be taken specifying the **k**-point mesh. While of course, the quality of the results increases with the resolution of the grid, the computational time of the background BoltzTraP calculations does so, too, and may be of the order of an hour (or much more for larger unit cells) for meshes with a spacing of the order of 0.1 Å^{-1} (as selected for the results shown below).
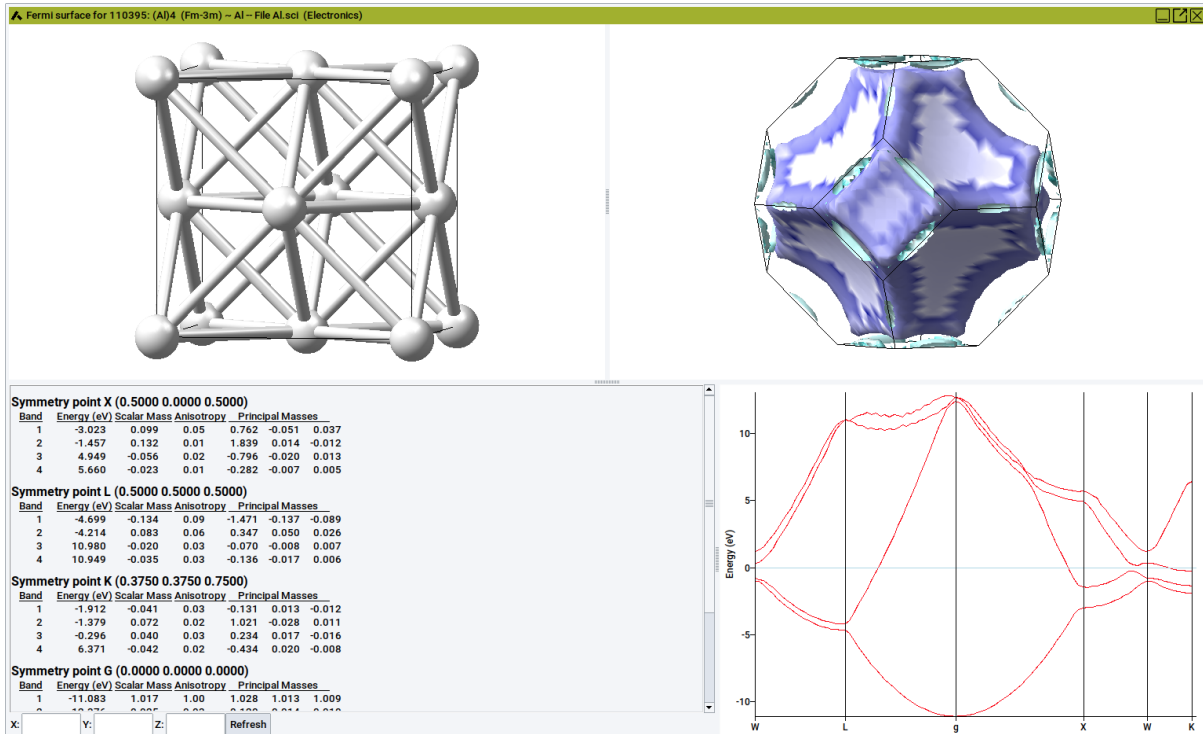
Finally, the Task frame allows specifying the particular Action to be taken. Here a choice can be made between Run all , Calculate Fermi surface only , and Recalculate electronic transport . The latter option is useful if the BoltzTraP calculation should be redone with a new range of chemical potentials or a new set of temperatures.

Visualization of the calculated results distinguishes between the isoelectronic surfaces and the electronic transport properties. To visualize an isoenergy surface, choose Fermi Surface from the Electronics menu and select results from a completed job.
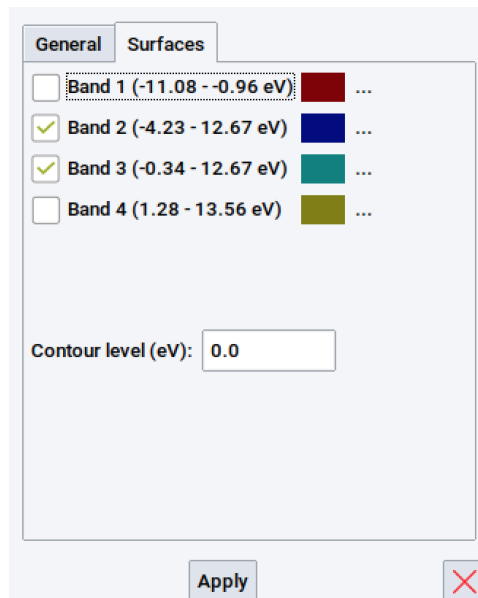
1 Fermi Surface

For the Fermi Surface a new window will open, which splits into four parts: The top row shows the structure (left) and the reciprocal cell, i.e. the first Brillouin zone (right). For metals, the reciprocal cell window displays also the Fermi surface. The bottom row displays numerical results per **k**-point and band (left) and the band structure plot (right). Note that the latter comprises only a limited number of bands within a rather narrow energy window around the Fermi energy. In addition, this band structure arises from projecting the electronic energies as calculated on the pre-specified regular **k**-point grid to the so-called high-symmetry lines. This is different from calculating the band structure directly from the VASP interface, which invokes direct calculation of the electronic energies at the **k**-points aligned along the high-symmetry lines and thus can return a more accurate band structure.

[1] Georg K H Madsen and David J Singh, "BoltzTraP. a Code for Calculating Band-Structure Dependent Quantities," Computer Physics Communications 175, no. 1 (July 2006): 67-71.

Symmetry point X (0.5000 0.0000 0.5000)

Band	Energy (eV)	Scalar Mass	Anisotropy	Principal Masses		
1	-3.023	0.099	0.05	0.762	-0.051	0.037
2	-1.457	0.132	0.01	1.839	0.014	-0.012
3	4.949	-0.056	0.02	-0.796	-0.020	0.013
4	5.660	-0.023	0.01	-0.282	-0.007	0.005

Symmetry point L (0.5000 0.5000 0.5000)

Band	Energy (eV)	Scalar Mass	Anisotropy	Principal Masses		
1	-4.699	-0.134	0.09	-1.471	-0.137	-0.089
2	-4.214	0.083	0.06	0.347	0.050	0.026
3	10.980	-0.020	0.03	-0.070	-0.008	0.007
4	10.949	-0.035	0.03	-0.136	-0.017	0.006

Symmetry point K (0.3750 0.3750 0.7500)

Band	Energy (eV)	Scalar Mass	Anisotropy	Principal Masses		
1	-1.912	-0.041	0.03	-0.131	0.013	-0.012
2	-1.379	0.072	0.02	1.021	-0.028	0.011
3	-0.296	0.040	0.03	0.234	0.017	-0.016
4	6.371	-0.042	0.02	-0.434	0.020	-0.008

Symmetry point G (0.0000 0.0000 0.0000)

Band	Energy (eV)	Scalar Mass	Anisotropy	Principal Masses		
1	-11.083	1.017	1.00	1.028	1.013	1.009

In the Fermi Surface visualization window, display of the isoenergy surfaces within the reciprocal cell still offers several options. Of course, the reciprocal cell with the isoenergy surface can be rotated and zoomed just as the real space structure. In addition, the gear icon showing when the cursor is moved to the top center of that window gives access to 3D rendering options, again in the same way as for the real space structure. Yet, the dialog opening after selecting the gear icon offers also a tab named Surfaces, which allows to adapt the contour level, i.e., the energy of the isoenergy surface, relative to the Fermi energy. Furthermore, each of the bands contributing at this energy can be selected or unselected for display and the color of the respective isoenergy surface can be specified.

To facilitate selection, the dialog reports the highest and lowest energy for each band. As a default, the contour level is set to zero and all bands straddling the Fermi energy are included. Hence, for semiconductors and insulators no surfaces are displayed by default. For aluminum, the example alcreated shown above, the Fermi surfaces of the two bands at the Fermi energy are displayed in the figures below.
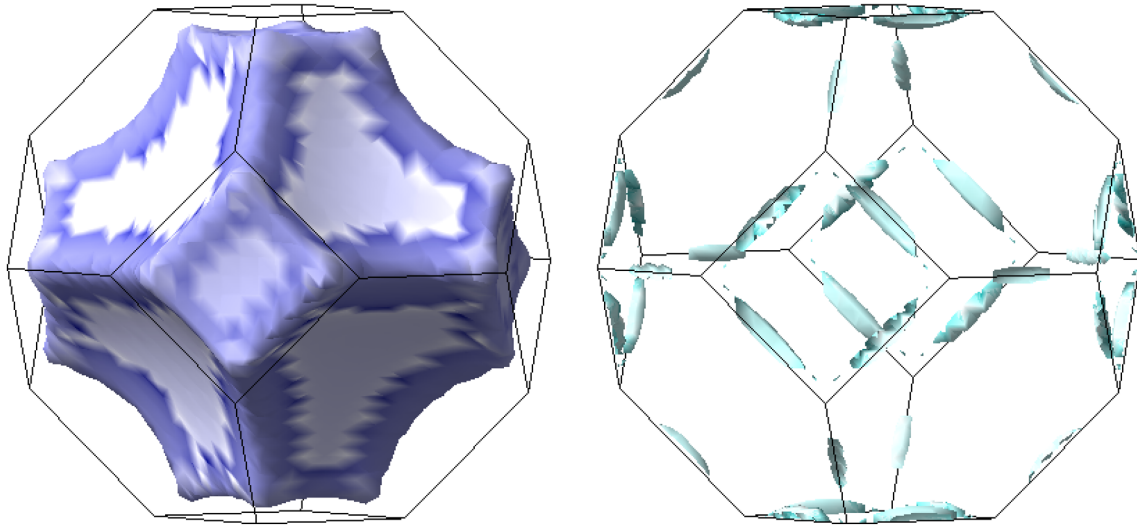
Moving the mouse over the Fermi surface graph displays information on mass, velocity, and speed of the **k**-point under the mouse pointer in the right part of the status bar at the bottom of the window, while the left part of the status bar gives the band number and **k**-point.

Approximate Effective Masses

In the lower-left part of the Fermi Surface visualization window, some numerical results are printed for a selected set of bands at the high-symmetry points (defining the high-symmetry lines used in the band structure plot at the lower right). They are based on the so-called effective mass tensor, which is given by

$$m_{\alpha\beta}^{-1} = \frac{\partial^2 \epsilon_n(k)}{\partial k_\alpha \partial k_\beta} \tag{1}$$

i.e. the curvature of a band at a particular **k**-point. The printed quantities include

- energy and scalar mass (geometric mean of the principal masses m_i, which are the eigenvalues of the effective mass tensor) multiplied by the degeneracy factor $g^{\frac{2}{3}}$

$$m = g^{\frac{2}{3}} \sqrt[3]{m_1 m_2 m_3} \tag{2}$$

- mass anisotropy

$$\Delta M = \sqrt{\frac{m_1}{m_2 m_3}} \quad \text{with} \quad m_1 \geq m_2 \geq m_3 \tag{3}$$

- principal masses, *i.e.* the eigenvalues of the effective mass tensor

**Note:** Note that for calculating conductivity in the Drude model the *effective mass m^** is defined as

$$m^* = \frac{3}{\sum\limits_{\alpha} \frac{1}{m_\alpha}} \tag{4}$$

To print these quantities at arbitrary **k**-points, specify and (custom) that **k**-point using the three entry fields: X: ____ Y: ____ Z: ____ and confirm with Refresh . To restore the printing of these quantities at the high-symmetry points just blank out the three entry fields and press the Refresh button again.

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2 Electronic Transport

To visualize the results of the electronic transport calculations as covered by the BoltzTraP code, choose Electronic Transport from the Electronics menu and select the completed job.

This will open a new window, which comprises a graphical display and several option entries and choices. Initially, the graphical display shows the trace of the electrical conductivity tensor as a function of temperature for several values of the chemical potential (in eV relative to the Fermi energy), which are displayed right to the graph (Chem. Pot.). By dragging the mouse pointer across the various values of the chemical potential, they turn red and the respective curve is highlighted.
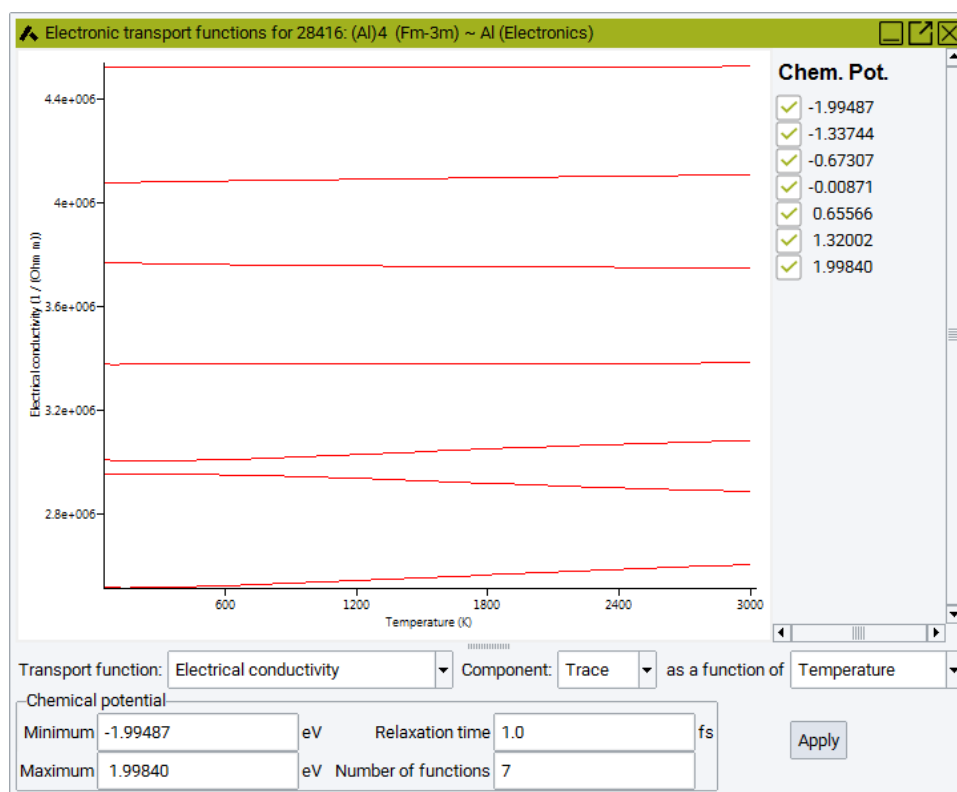

In the lower part of the window, display of the Electrical Conductivity can be replaced by one of the following: Rigid band doping , Carrier density , Density of states (at the Fermi energy), Seebeck coefficient (or thermoelectric power), Carrier mobility , Inverse transport effective mass , Electronic fitness function , Hall coefficient , the electronic contribution to the Thermal conductivity , Electronic specific heat , or Pauli paramagnetic susceptibility . In addition, the Component of the corresponding tensor or else its Trace can be selected. Finally, all these quantities can be displayed as a function of Temperature (at different values of the chemical potential), as a function of Chemical Potential (at different values of the temperature) or as a function of Carrier density (at different values of the temperature). Depending on this choice, Minimum and Maximum values for either the chemical potential or the temperature, as well as the Number of functions to be displayed can be selected.

Finally, some of the quantities to be displayed still depend on the choice of the so-called Relaxation time , which can be set in the corresponding entry field. In this context, it should be noted that BoltzTraP relies on the relaxation-time approximation, which replaces the relaxation time, which in general depends on $\mathbf{k}$-vector and band, by a single value, which is the same at all $\mathbf{k}$-points and for all bands. While for some quantities as, e.g., the Seebeck coefficient , the so approximated relaxation time cancels out, it still enters other quantities as a linear prefactor. This applies to the Electrical Conductivity , the Carrier mobility , and the electronic contribution to the Thermal conductivity . In contrast, in addition to the Seebeck coefficient , the Rigid band doping , Carrier density , Density of states at the Fermi energy,

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Inverse transport effective mass , Electronic fitness function , Hall coefficient , Electronic specific heat , and Pauli paramagnetic susceptibility are independent of the relaxation time.

Any change of the four input parameters grouped in the frame need to be applied either by pushing the Apply button, or by changing the Transport function , their Component or the x-axis definition (as a function of), to become effective in the graph.

As examples, the figures below display the electronic specific heat (left) and the paramagnetic susceptibility of Al (right), which as expected show the almost linear dependence on temperature and the nearly temperature-independent behavior, respectively.
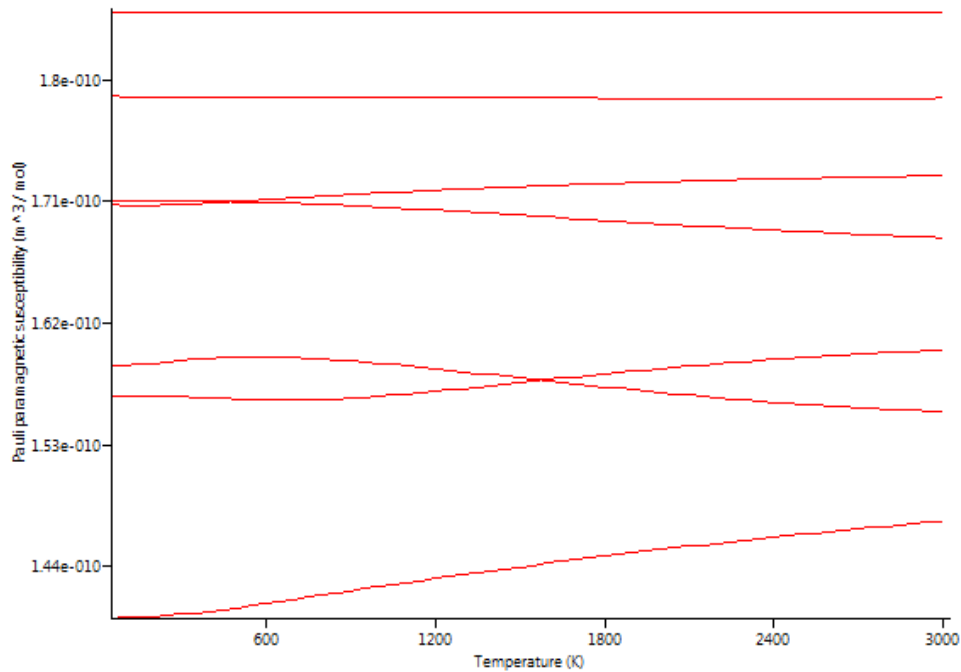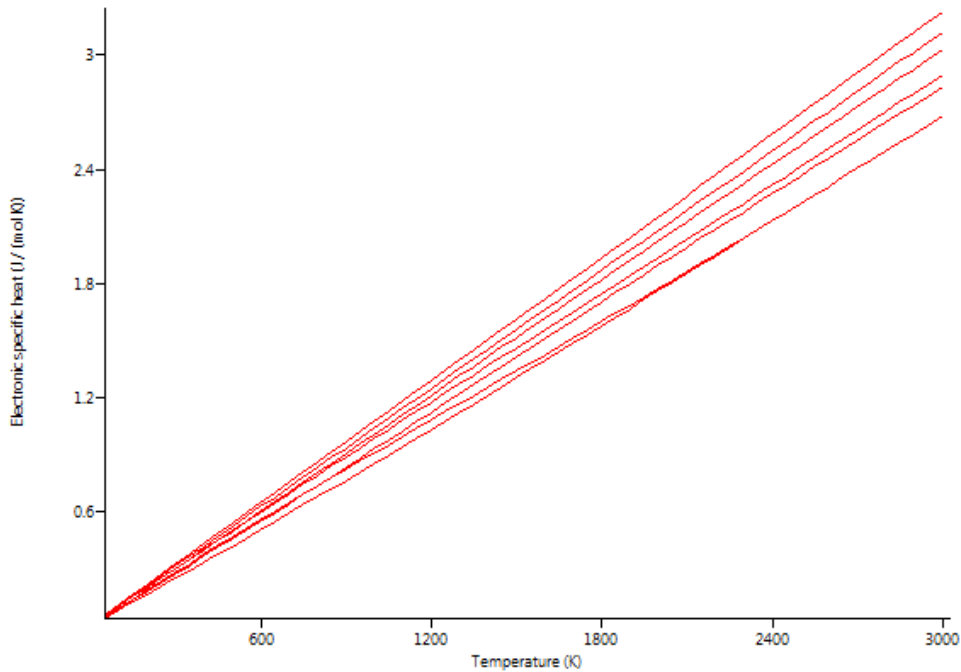
3 Accurate Effective Masses

In addition to allowing access to the Fermi surface and the transport properties, *Electronics* provides an alternative means to compute high-accuracy effective masses, which is based on zooming into specified **k**-points and the use of a fine local **k**-mesh. The latter is a fine grid of **k**-points centered about the **k**-point of interest and usually consisting of 3x3x3, 5x5x5, or 7x7x7 points. Calculated energy states at these grid points are fed into a highly-efficient non-linear least-squares fit, from which the so-called effective mass tensor is extracted. Diagonalization of the effective mass tensor then yields the principle masses according to the formulas noted above.

This functionality can be accessed via the Jobs >> New Job... menu item. In this menu, add to the Start stage a VASP calculation by clicking VASP 6: Density Functional Theory (or any other VASP version) from the Methods section, and Effective Mass from the General Properties section on the right-hand side of the window. As a result, the following Flowchart is obtained.
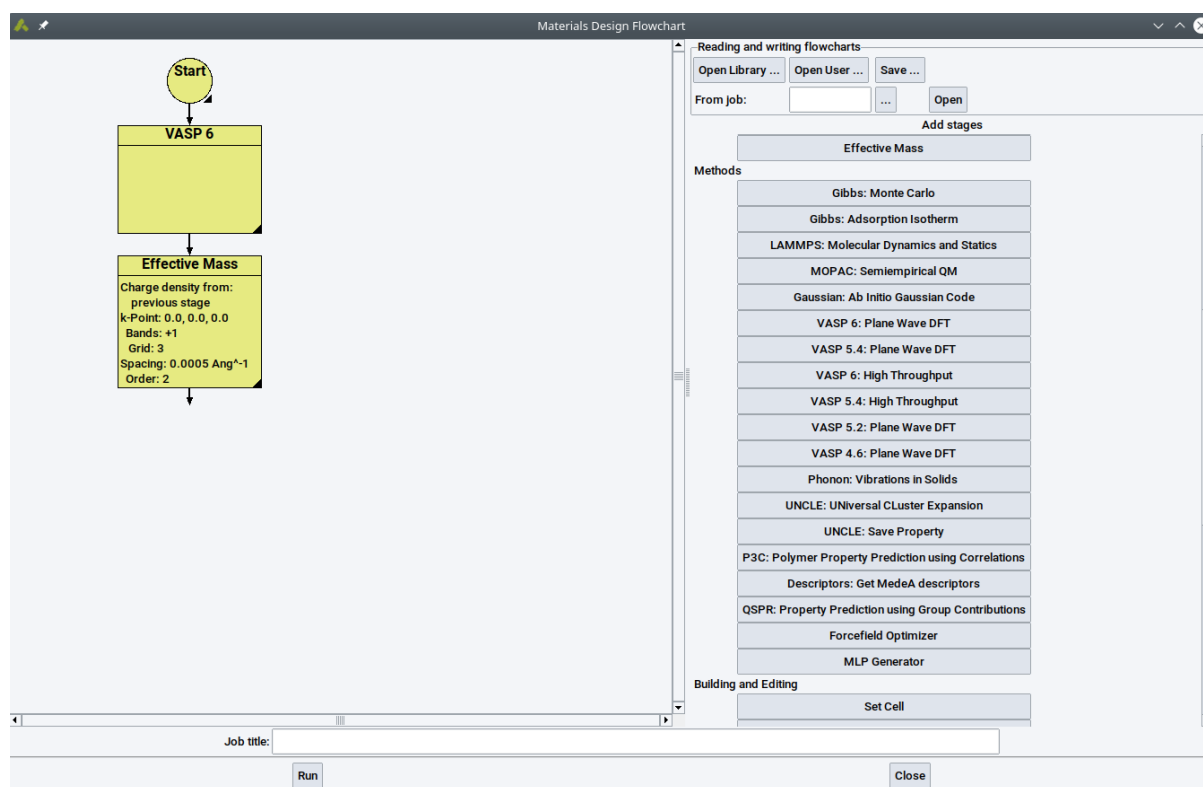

Still, the single stages need some attention. As described before, double-clicking the VASP 6 stage allows adapting the parameters of the VASP calculation. Two points are particularly noteworthy. First, click the box (Pseudo, difference, spin) charge density as indicated in the following figure since the subsequent Effective Mass stage will need the charge density as input.

Second, the calculation of correct effective masses requires a highly accurate potential created at this stage of the calculation. For this reason, make sure that the **k**-point mesh is fine enough and does not go below normal precision or the default plane-wave cutoff. It is proposed to adapt these important parameters until converged results for the effective masses are obtained. Here, the *MedeA Automated Convergence* tool can be helpful.
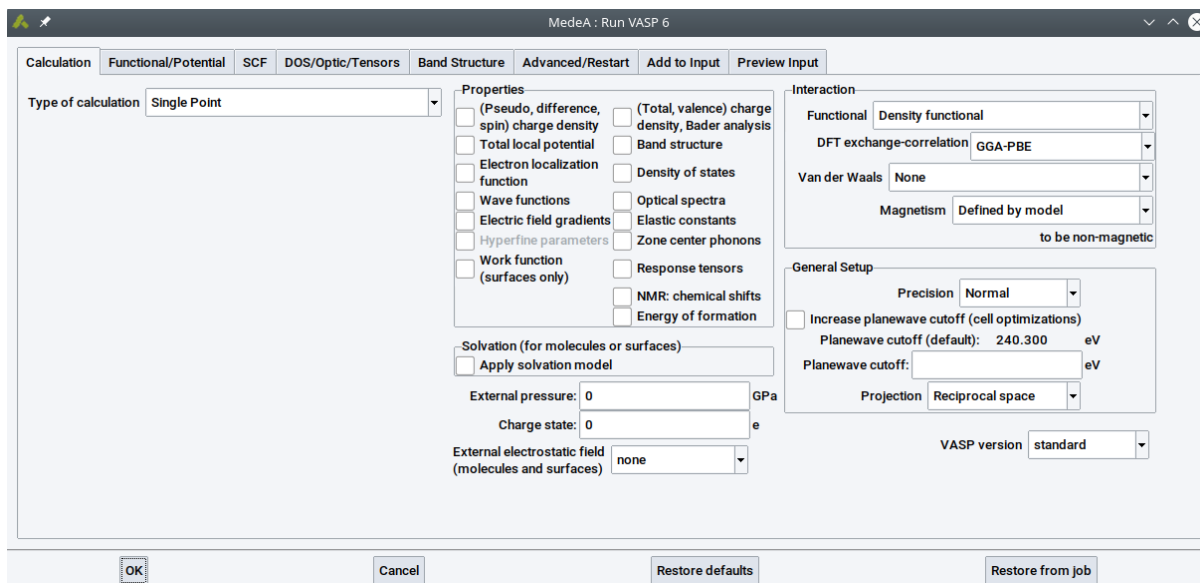
In the same way, as for the VASP 6 stage, double-clicking the Effective Mass stage opens a new dialog window as is shown below, which can be used to access the full functionality of the Effective Mass calculation. In particular, the **k**-point, at which the effective mass(es) will be calculated, has to be selected as well as the range of Bands to be included in the calculation. Furthermore, the Grid size can be specified (e.g., 5x5x5 as in the example shown below) and the Grid spacing of the local grid. For the Order of fit, while a 2$^{\text{nd}}$ order fit will suffice for most bands, even up to 4$^{\text{th}}$ order fits can be performed. Finally, the dialog allows specifying whether to use symmetry, whether to keep the Gamma point in Gamma centered grids, and whether to Offset the grid by a certain distance in reciprocal Angstrom units away from its default centering about the **k**-point specified before.
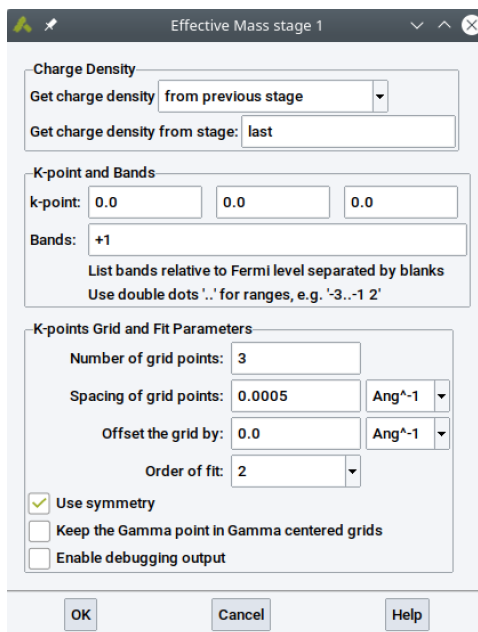
The results of the analysis of the electronic bands are written to the file *Job.out*. There, for each band in the requested range RMS (root mean square) values for the non-linear least-squares fit are given together with the fitted band energy, the effective mass tensor, and the resulting principal masses. Finally, most of these data are summarized at the end in the form of a small table for better readability. The calculation of accurate effective masses requires well converged electronic bands and well-adapted local **k**-point grids. For this reason, please check your results concerning an optimal setting of all calculation parameters.