First Principle 2017-Fall midterm Solution

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1. Al band structure using GGA calculation and free-electron band structure.

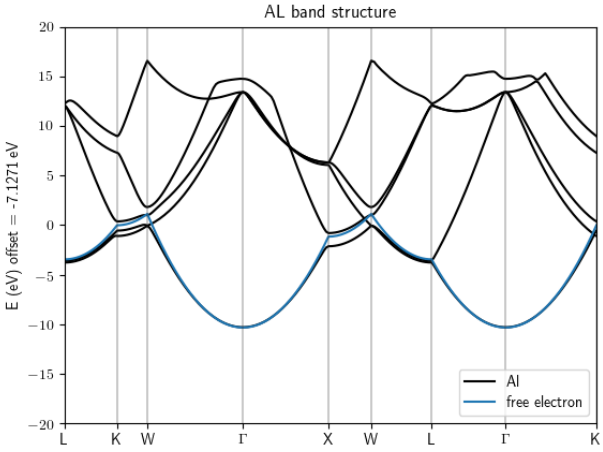

FIG. 1. Al band structure and free-electron band

In match the free electron band, we have to consider also the work function W (or equivalent the vacuum potential) of Al, in which the calculation gives : $W_{Al} = 3.207eV$

2. Consider 1D case of KS ansatz. To derive the KS potential from the known density, we start with KS equation:

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial x^2} + v_s(x)\right]\phi_i(x) = \epsilon_i\phi_i(x) \tag{1}$$

In here we set $\hbar$ and mass m as 1.

Since there is a freedom to choose the basis, we can choose a basis that is real such that $\phi_i^* = \phi_i$. In

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which we can express the density and the kinetic density τ_L and τ as :

$$\rho(x) = \sum_i \phi(x)^2 \tag{2}$$

$$\tau_L = -\frac{1}{2}\sum_i \phi_i(x)\frac{\partial^2}{\partial x^2}\phi_i(x) \tag{3}$$

$$\tau = \frac{1}{2}\sum_i |\frac{\partial}{\partial x}\phi_i(x)|^2 \tag{4}$$

$$\tau_L = \tau - \frac{1}{4}\frac{\partial^2}{\partial x^2}\rho(x) \tag{5}$$

First, we multiply KS equation with ϕ_i and sum over i:

$$\tau_L + v_s(x)\rho(x) = \sum_i \epsilon_i \phi_i(x)^2 \tag{6}$$

then take derivation:

$$\frac{\partial}{\partial x}\tau_L + v_s(x)\frac{\partial}{\partial x}\rho(x) + \rho(x)\frac{\partial}{\partial x}v_s(x) = 2\sum_i \epsilon_i\phi_i(x)\frac{\partial}{\partial x}\phi_i(x) \tag{7}$$

Now return to equation (1) and multiply by $2\frac{\partial}{\partial x}\phi_i(x)$ and sum over i:

$$-\sum_i \frac{\partial^2}{\partial x^2}\phi_i(x)\frac{\partial}{\partial x}\phi_i(x) + v_s(x)\frac{\partial}{\partial x}\rho(x) = 2\sum_i \epsilon_i\phi_i(x)\frac{\partial}{\partial x}\phi_i(x) \tag{8}$$

combine with equation (7) and (8), we have :

$$\frac{\partial}{\partial x}\tau_L + \sum_i \frac{\partial^2}{\partial x^2}\phi_i(x)\frac{\partial}{\partial x}\phi_i(x) + \rho(x)\frac{\partial}{\partial x}v_s(x) \tag{9}$$

$$= \frac{\partial}{\partial x}\tau_L + \frac{\partial}{\partial x}\tau + \rho(x)\frac{\partial}{\partial x}v_s(x) = 0 \tag{10}$$

With given density $\rho(x)$:

$$\rho(x) = Ae^{-\alpha x^2} \tag{11}$$

the kinetic energy densities are obtained:

$$\tau = \frac{1}{2}A\alpha^2 x^2 e^{-\alpha x^2} \tag{12}$$

$$\tau_L = \frac{A\alpha}{2}e^{-\alpha x^2}\left[1 - \alpha x^2\right] \tag{13}$$

insert (12),(13) into (10) we have :

$$\rho(x)\frac{\partial}{\partial x}v_s(x) = \alpha^2 x\rho(x) \tag{14}$$

Thus we have derived the potential with constant c:

$$v_s(x) = \frac{\alpha^2}{2}x^2 + c \tag{15}$$

Finally, the normalization constant A can be derived with :

$$\int_{-\infty}^{\infty} \rho(x) = 1 \tag{16}$$

$$A\int_{-\infty}^{\infty} e^{-\alpha x^2} = A\sqrt{\frac{\pi}{\alpha}} = 1 \tag{17}$$

$$A = \sqrt{\frac{\alpha}{\pi}} \tag{18}$$

3. Car-Parrinelo EOM

The Car-Parrinelo lagrangian:

$$L = \sum_i \frac{1}{2}\mu \int |\dot{\phi}_i(r)|^2 dr + \sum_I \frac{1}{2} M_I \dot{R_I}^2 - E\left[\phi_i, R_i\right] - \sum_{ij} \Lambda_{ij} \int \phi_i(r)\phi_j(r)dr - \delta_{ij} \tag{19}$$

To impose the orthonmality, we add a term with lagrangian multiplier Λ_{ij}. With the Euler-Lagrangian equation:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}} = \frac{\partial L}{\partial q} \tag{20}$$

The equation of motion of electronic and ionic DOF can be derived as:

$$\mu\ddot{\phi}_i(r) = -\sum_j \Lambda_{ij}\phi_j(r) - \frac{\partial E[\phi_i, R_I]}{\partial \phi_i} \tag{21}$$

$$M_I\ddot{R}_I = \frac{-\partial E[\phi_i, R_I]}{\partial R_I} \tag{22}$$

4. GGA, GGA+U of MnO in AF-II The crystal and magnetic structure of MnO in AF-II:

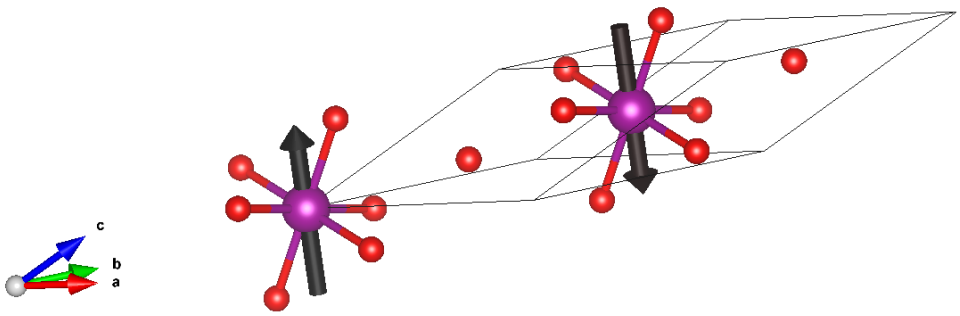

FIG. 2. MnO in AF-II, (**purple**: *Mn* atoms carry magnetic moment; **red**: non-magnetic *O* atoms)

- GGA

  (1) the band structure and total DOS, the energies are shifted by fermi energy $E_f = 5.2304eV$ to zero.

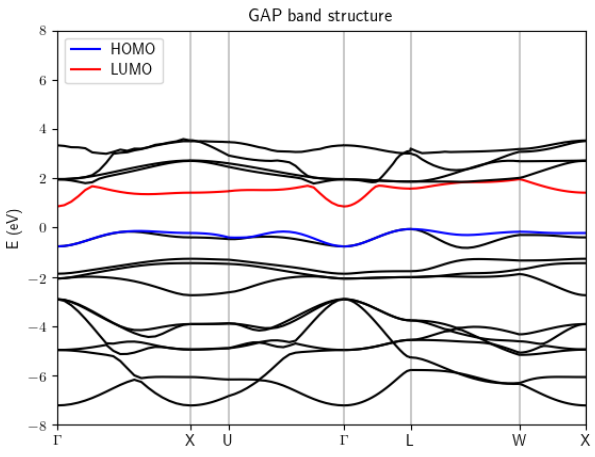

FIG. 3. MnO-AFII band-structure

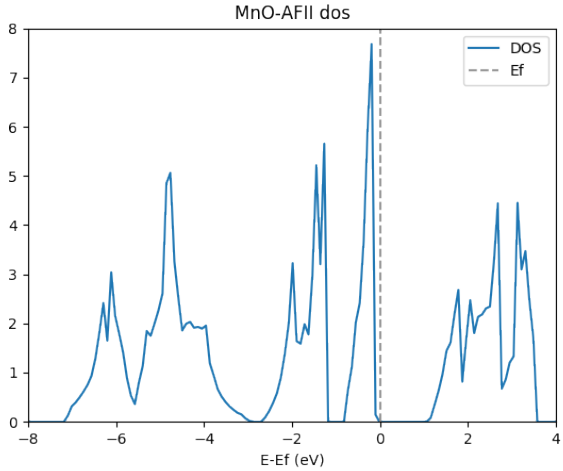

FIG. 4. MnO-AFII density of state

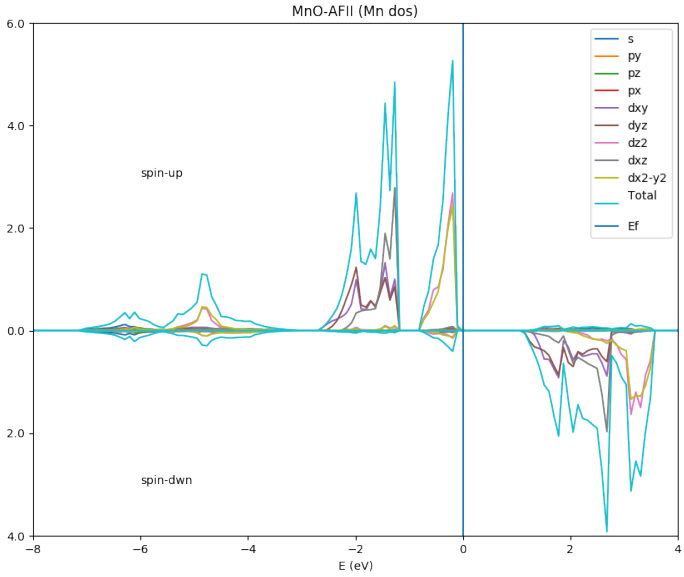

FIG. 5. Mn in MnO density of state

Energy gap E_g ,total magnetic moment m and Mn moment m_{Mn}:

$$E_g = 0.918700eV$$
$$m = 0.0000\mu_B$$
$$m_{Mn} = 4.199\mu_B$$

- GGA+U

  (1) the band structure and total DOS, the energies are shifted by fermi energy $E_f = 4.0271/eV$ to zero.

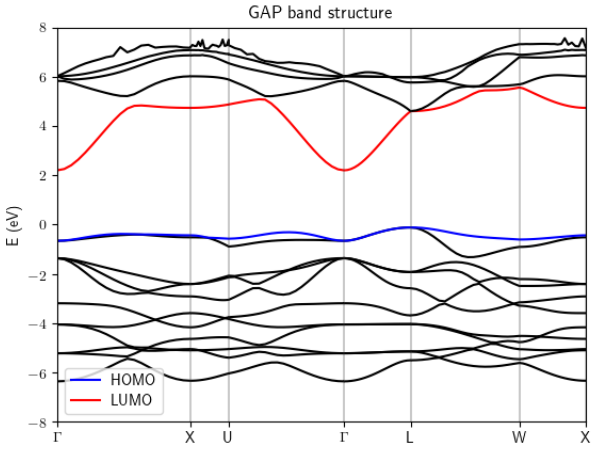

FIG. 6. MnO-AFII band-structure GGA+U

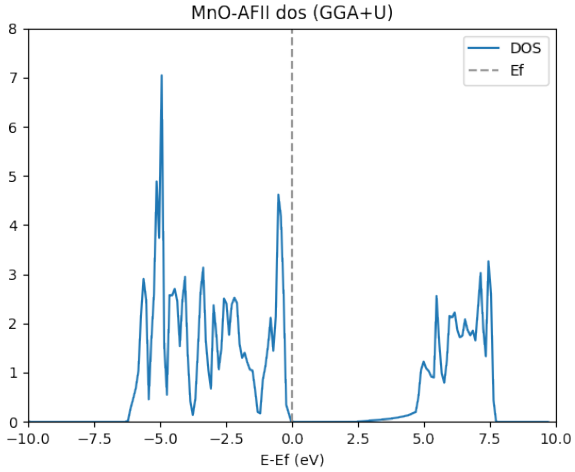

FIG. 7. MnO-AFII density of state GGA+U

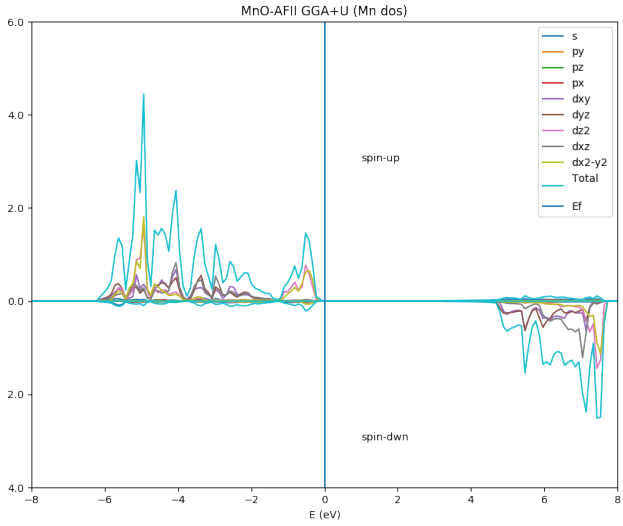

FIG. 8. Mn in MnO density of state GGA+U

Energy gap E_g ,total magnetic moment m and Mn moment m_{Mn}:

$$E_g = 2.318900eV$$
$$m = 0.0000\mu_B$$
$$m_{Mn} = 4.686\mu_B$$

By apply U_{eff} on Mn, we decouple the Mn and O energy part, as a result, the AF magnetic property contributed form Mn can be calculate more accurate.

5. Finite difference algorithms.

   In the following, we evaluate the harmonic oscillator with "Euler" , "Predictor-Corrector" and "Velocity-verlet" method.

   (a) Euler method with different dt (in unit of π) for initial condition $x(0) = 1$,$v(0) = 0$:

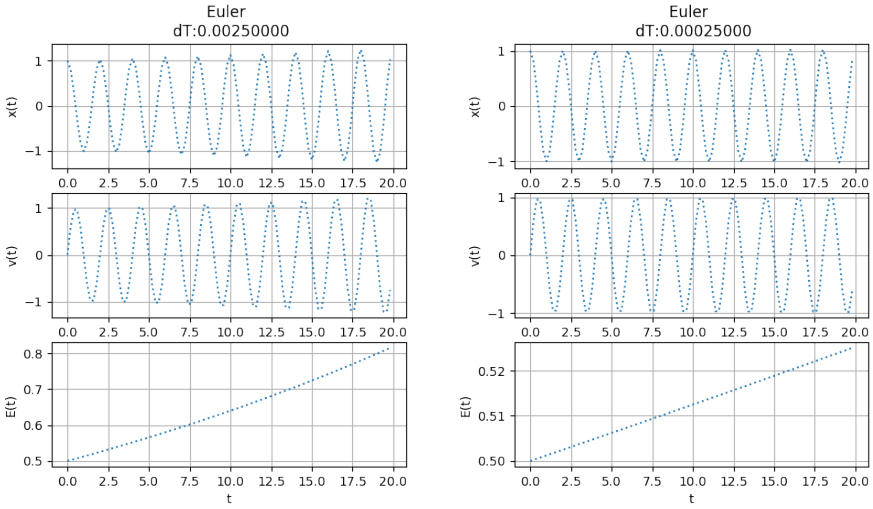

FIG. 9. Euler method, $dt = 2.5 \times 10^{-3}(left)$ and $dt = 2.5 \times 10^{-4}(right)$

compare the result with (a), we can see that reducing the update time interval, the energy still not conserved, but the error is decreased.

(b) Euler method compare with Predictor-Corrector method with $dt = 2.5 \times 10^{-3}$ (in unit of π), $x(0) = 1$,$v(0) = 0$

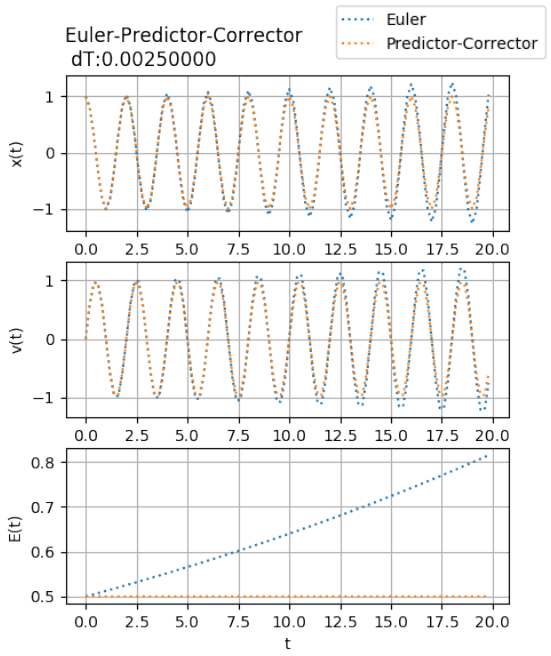

FIG. 10. Euler v.s. Predictor-Corrector method , $dt = 2.5 \times 10^{-3}$

compare the result with (a), we can see that with the same update time interval (dt), we can see that the energy increment error is significantly reduced.

(c) Euler method compare with Velocity-Verlet method with $dt = 2.5 \times 10^{-3}$ (in unit of π), $x(0) = 1$,$v(0) = 0$

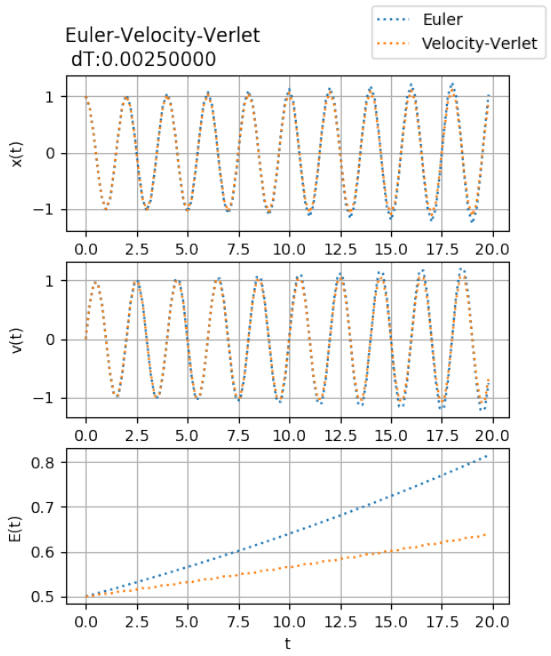

FIG. 11. Euler v.s. Velocity-Verlet method , $dt = 2.5 \times 10^{-3}$

compare the result with (a), we can see that with the same update time interval (dt), we can see that the energy increment error is reduced.