Advanced Materials Modeling
Beyond DFT 1

+ Many-body physics
+ The total energy : Quantum monte Carlo
+ Experiments : total energy, band gap, spectroscopies ?
+ Charged excitations and Green's function G
+ GW approximation (incl. self-consistency and miscellaneous tricks)

A basic reference on first-principles simulations of Interacting electrons

Richard M. Martin, L. Reining, and D.M. Cepreley

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Interacting electrons:

Theory and computational approaches

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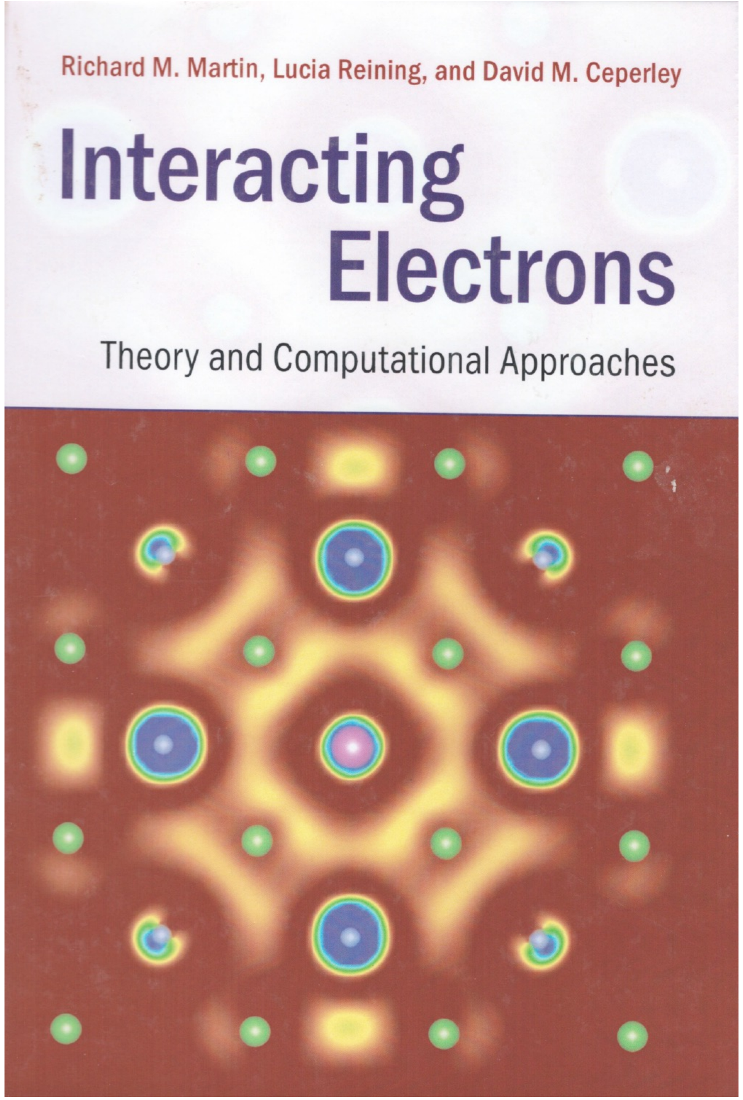


Richard M. Martin, Lucia Reining, and David M. Ceperley

Interacting Electrons

Theory and Computational Approaches

Many-body physics

Systems with n electrons and N nuclei

- Born-Oppenheimer approximation.
- Nuclei are treated as distinct particles, without spin. Internal structure is neglected. Only charge, mass and (classical) position taken into account.

Wavefunction :

$$\Psi_e(\mathbf{r}_1,\sigma_1,\mathbf{r}_2,\sigma_2,\ldots,\mathbf{r}_n,\sigma_n;\mathbf{R}_1,\mathbf{R}_2,\ldots\mathbf{R}_N)$$ + antisymmetry for electron exchange

Electronic Hamiltonian, in atomic units (without spin-orbit) :

$$\hat{T}_e = \sum_{i=1}^{n} -\frac{\nabla_{r_i}^2}{2} \qquad \hat{V}_{eN} = \sum_{A}^{N} \sum_{i}^{n} \frac{-Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \qquad \hat{V}_{ee} = \sum_{\substack{(i,j)\\ i<j}}^{(n,n)} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$\hat{H}_e = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee}$$

$$\boxed{\hat{H}_e|\Psi_e\rangle = E_e|\Psi_e\rangle}$$

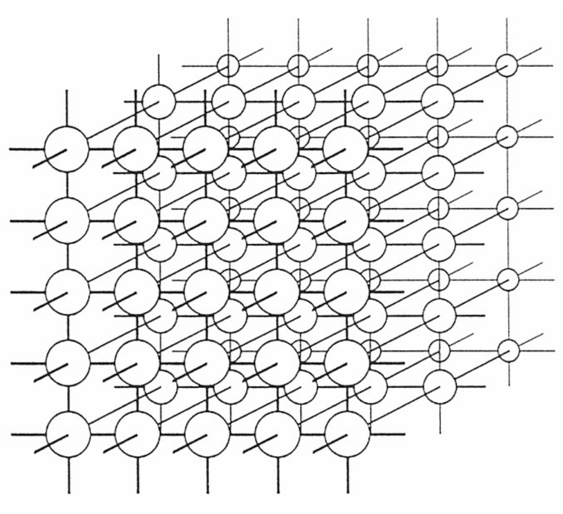
Many-body wavefunction representation

Classical objets : fields $p(\mathbf{r},t), V(\mathbf{r},t), T(\mathbf{r},t), \mathbf{E}(\mathbf{r},t), \ldots$

or trajectories $\mathbf{R}_1(t), \mathbf{R}_2(t), \mathbf{R}_3(t), \ldots \mathbf{R}_N(t)$

Quantum objects : wavefunctions

for interacting particles $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N, t)$



Classical position and speed of 8 objects
2x3x8=48 real numbers.

Oxygen atom : 8 electrons.
Quantum description, on a cubic grid of 10x10x10 points.
24-dimensional object => 10^{24} complex numbers

HF, DFT : set of wavefunctions for non-interacting particles

For the oxygen atom, back to 8x10x10x10 real numbers,
but with an approximate treatment ...

Simplified notations

(1) Arguments of wavefunction :

$$\Psi_e(\mathbf{r}_1,\sigma_1;\mathbf{r}_2,\sigma_2;\ldots;\mathbf{r}_n,\sigma_n) \Longrightarrow \Psi_e(1,2,\ldots,n)$$

"1" becomes a symbol to denote $\mathbf{r}_1,\sigma_1$

(2) Define also $r_{ij} \triangleq |\mathbf{r}_i-\mathbf{r}_j|$

$$\hat{V}_{ee} = \sum_{\substack{(i,j)\\ i<j}}^{(n,n)} \frac{1}{r_{ij}}$$

and "one-particle" part of Hamitonian

$$\hat{V}_{eN} = \sum_{A}^{N}\sum_{i}^{n}\frac{-Z_A}{r_{iA}} = \sum_{i}^{n}\hat{V}_N(\mathbf{r}_i)$$

$$\hat{h}^N(i) \triangleq -\frac{\nabla_{r_i}^2}{2} + \hat{V}_N(\mathbf{r}_i)$$

Hamitonian becomes :

$$\left(\sum_{i}^{n}\hat{h}^N(i) + \sum_{\substack{(i,j)\\ i<j}}^{(n,n)}\frac{1}{r_{ij}}\right)\Psi_e(1,2,\ldots,n) = E_e\Psi_e(1,2,\ldots,n)$$

Separation of variables

$$\left(\sum_{i}^{n} \hat{h}^{N}(i) + \boxed{\sum_{\substack{(i,j)\\ i<j}}^{(n,n)} \frac{1}{r_{ij}}}\right)\Psi_{e}(1,2,\ldots,n) = E_{e}\,\Psi_{e}(1,2,\ldots,n)$$

+ antisymmetry for electron exchange

Interelectronic coupling does not
allow to separate electronic coordinates

Mean-field approximation (like DFT)

$\sum_{\substack{(i,j)\\ i<j}}^{(n,n)} \frac{1}{r_{ij}}$ replaced by $\sum_{i} \hat{V}_{Hxc}(i)$

$$\hat{h}^{N}_{MF}(i) = \hat{h}^{N}(i) + \hat{V}_{Hxc}(i)$$

$$\left(\sum_{i}^{n} \hat{h}^{N}_{MF}(i)\right)\Psi_{MF,e}(1,2,\ldots,n) = E_{MF}\,\Psi_{MF,e}(1,2,\ldots,n)$$

+ antisymmetry for electron exchange

gives solutions as
Slater determinants of 1-particle wavefunctions
mean-field energy=sum of 1-particle eigenenergies,
must be corrected to give electronic energy (avoid double-counting)

Monte Carlo approaches

$$\left(\sum_{i}^{n}\hat{h}^{N}(i)+\boxed{\sum_{\substack{(i,j)\\ i<j}}^{(n,n)}\frac{1}{r_{ij}}}\right)\Psi_{e}(1,2,\ldots,n)=E_{e}\,\Psi_{e}(1,2,\ldots,n)$$

Variational Monte Carlo
Diffusion Monte Carlo
Diagrammatic Monte Carlo
Green’s function Monte Carlo
…

“Monte Carlo” refers to stochastic evaluation of high-dimensional integrals using random sampling, and generation of such samplings using random walks

Usually : target evaluation of the ground-state energy

Monte Carlo approaches (brief overview)

Variational Monte Carlo (VMC)

$$\hat{H}_e \Psi_e(1,2,\ldots,n) = \left(\sum_i^n \hat{h}^N(i) + \boxed{\sum_{\substack{(i,j)\\ i<j}}^{(n,n)} \frac{1}{r_{ij}}} \right) \Psi_e(1,2,\ldots,n) = E_e \Psi_e(1,2,\ldots,n)$$

Use the variational principle to approximate ground-state energy

$$E_{e,GS} = \min_{\Psi_e \text{ normalized}} \left\langle \Psi_e \middle| \hat{H}_e \middle| \Psi_e \right\rangle < E_{e,trial} = \left\langle \Psi_{e,trial} \middle| \hat{H}_e \middle| \Psi_{e,trial} \right\rangle$$

Simplest form of VMC : use trial wavefunctions of the type

$$\Psi_{e,trial}(1,2,\ldots,n) = \left(\prod_{\substack{(i,j)\\ i<j}}^{(n,n)} f(r_{ij}) \right) \Psi_{SD}(1,2,\ldots,n)$$

Jastrow-Slater

Jastrow factor, symmetric upon electron exchange, builds-in correlation between electrons
f tends to 1 at large separation, and to zero at small separation

Slater determinant, antisymmetric upon electron exchange

Challenge : multi-dimensional integrals

$$\left\langle \Psi_{e,trial} \middle| \hat{H}_e \middle| \Psi_{e,trial} \right\rangle \quad \text{with} \quad \hat{H}_e = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee}$$

$$\hat{T}_e = \sum_{i=1}^{n} -\frac{\nabla_{r_i}^2}{2} \qquad \hat{V}_{eN} = \sum_{A}^{N} \sum_{i}^{n} \frac{-Z_A}{\left|\mathbf{r}_i - \mathbf{R}_A\right|} \qquad \hat{V}_{ee} = \sum_{\substack{(i,j) \\ i<j}}^{(n,n)} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

$$\text{and} \quad \Psi_e(1,2,...,n) = \left(\prod_{\substack{(i,j) \\ i<j}}^{(n,n)} f(r_{ij}) \right) \Psi_{SD}(1,2,...,n)$$

$$\left\langle \Psi_{e,trial} \middle| \hat{H}_e \middle| \Psi_{e,trial} \right\rangle = \int \ldots \int \Psi^*_{e,trial}(1,\ldots N) \hat{H}_e \Psi^*_{e,trial}(1,\ldots N) d1 \ldots dN$$

No simple expression for the expectation value,
unlike with Slater determinants

Evaluation of Jastrow-Slater wavefunction energy expectation,
then optimization of orbitals of Slater determinant and Jastrow factor ?

Stochastic evaluation

$$\left\langle \Psi_{e,trial} \middle| \hat{H}_e \middle| \Psi_{e,trial} \right\rangle = \int \ldots \int \Psi^*_{e,trial}(1,\ldots N)\hat{H}_e \Psi^*_{e,trial}(1,\ldots N)d1\ldots dN$$

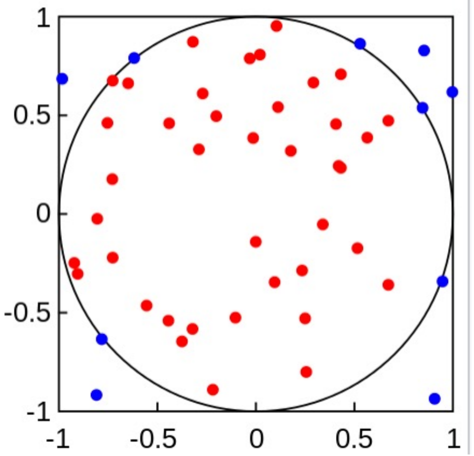
Standard multi (few) dimensional integration of dimention d :
sample with homogeneous grid of L points in each dimension,
with step h inversely proportional to L .

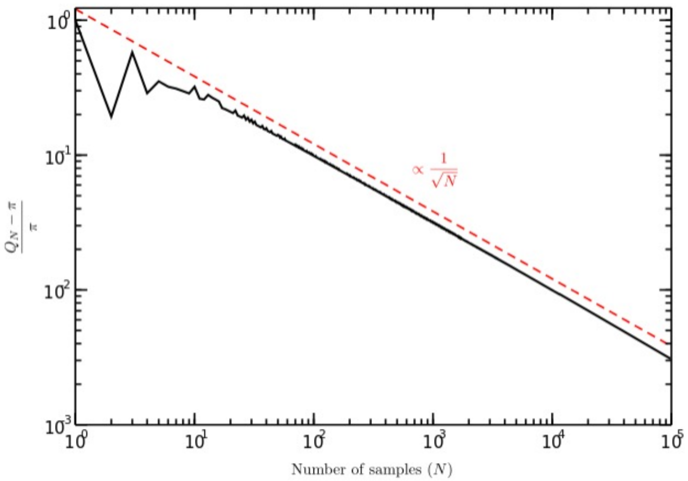
Total number of points $M{=}L^d$

Convergence of Simpson rule error $\varepsilon = (1/L)^4 = M^{-4/d}$

Random sampling $\varepsilon = M^{-1/2}$

Better than fixed grid
technique for $d > 8$!





Importance sampling

Sampling point distribution : generated from the trial wavefunction, to favour the configurations that have higher probability

$$\Pi(1\ldots N)=\frac{\left|\Psi_{e,trial}(1\ldots N)\right|^2}{\int\left|\Psi_{e,trial}(1\ldots N)\right|^2 d1\ldots dN}$$

Metropolis algorithm to generate a random walk in the multi-dimensional space $(1\ldots N)_i$ for $i=1 \ldots M$,
whose probability distribution tends to $\Pi(1\ldots N)$
by randomly generating new configurations and accepting/rejecting them

Then evaluate $$\left\langle\Psi_{e,trial}\middle|\hat{H}_e\middle|\Psi_{e,trial}\right\rangle=\lim_{M\to\infty}\frac{1}{M}\sum_{i=1}^{M}E_L\left((1\ldots N)_i\right)$$

where $$E_L\left((1\ldots N)\right)=\mathrm{Re}\frac{\hat{H}_e\Psi_{e,trial}(1\ldots N)}{\Psi_{e,trial}(1\ldots N)}$$

Diffusion Monte Carlo

Consider time-dependent Schrödinger equation in imaginary time

$$i\hbar\frac{\partial}{\partial t}\left|\Psi_e(t)\right\rangle=\hat{H}_e\left|\Psi_e(t)\right\rangle \qquad \Rightarrow \qquad -\hbar\frac{\partial}{\partial\tau}\left|\Psi_e(\tau)\right\rangle=\hat{H}_e\left|\Psi_e(\tau)\right\rangle$$

Propagate initial trial wavefunction $\left|\Psi_{e,trial}(\tau=0)\right\rangle$ using such Eq.

Complete set of eigenfunctions of Hamiltonian $\hat{H}_e\left|\Psi_i\right\rangle=E_i\left|\Psi_i\right\rangle$

Solve imaginary-time Schrödinger equation $\left|\Psi_i(\tau)\right\rangle=e^{-E_i\tau}\left|\Psi_i\right\rangle$

Decomposition of $\left|\Psi_{e,trial}(\tau=0)\right\rangle=\sum_{i=1}c_i\left|\Psi_i\right\rangle$

$$\left|\Psi_{e,trial}(\tau)\right\rangle=\sum_{i=1}c_ie^{-E_i\tau}\left|\Psi_i\right\rangle$$

Hence, in the large-time limit $\left|\Psi_{e,trial}(\tau)\right\rangle \rightarrow \left|\Psi_{e,i=\text{Ground State}}\right\rangle$

Diffusion Monte-Carlo = generate a random walk using imaginary-time Schrödinger equation

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Accuracy of Quantum Monte Carlo

Variational Monte Carlo :

quality of Energy estimate depends directly on trial wavefunction

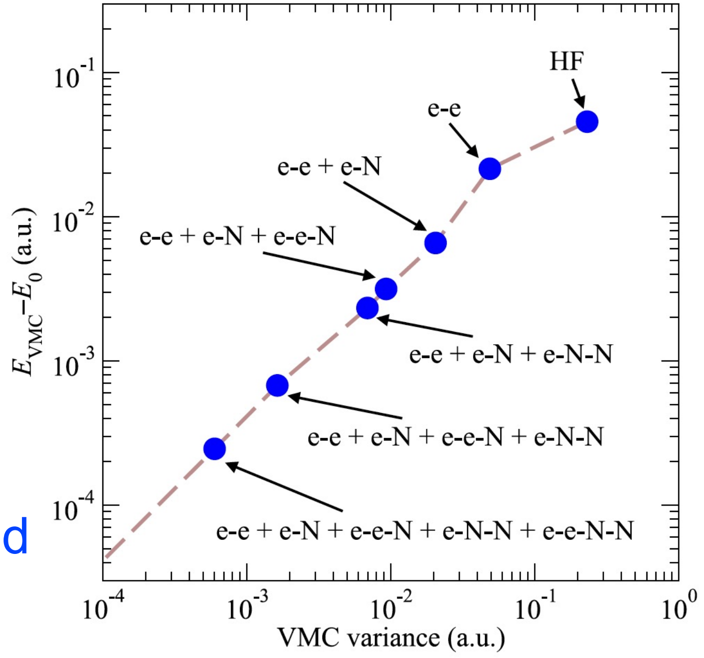
Diffusion Monte Carlo :

quality of Energy is partly dependent on trial wavefunction

Still not exact !

Indeed, the antisymmetry of the sampling of the random walk is hard to maintain => fixed-node approximation (and fixed-node error)

VMC H_2 benchmark : total energy difference wrt numerically exact results With improved Jastrow



NiO lattice parameter, cohesive energy

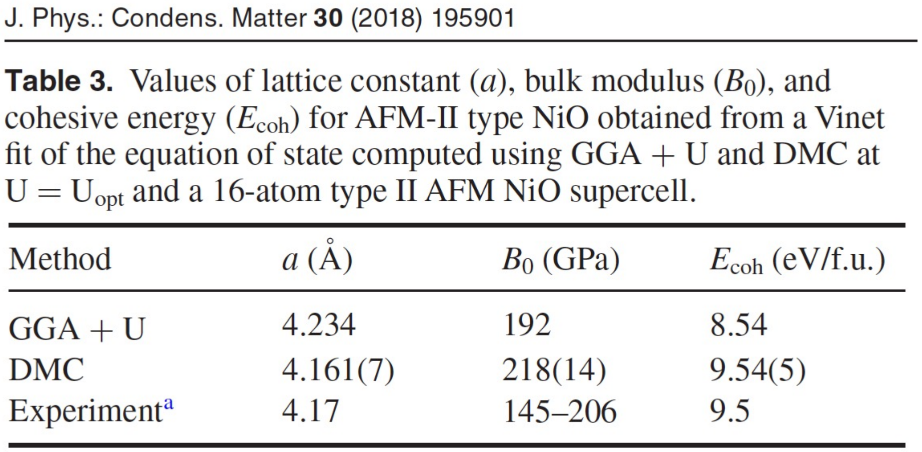


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Table 3. Values of lattice constant (a), bulk modulus (B_0), and cohesive energy (E_{coh}) for AFM-II type NiO obtained from a Vinet fit of the equation of state computed using GGA + U and DMC at $U = U_{opt}$ and a 16-atom type II AFM NiO supercell.

Method	a (Å)	B_0 (GPa)	E_{coh} (eV/f.u.)
GGA + U	4.234	192	8.54
DMC	4.161(7)	218(14)	9.54(5)
Experiment[a]	4.17	145–206	9.5

Early outcome of Quantum Monte Carlo

Accurate evaluation of exchange-correlation energy

Ceperley and Alder, Phys. Rev. Lett. 45, 566 (1980).

Basis of most DFT parameterizations (LDA, then GGA, hybrids, etc)

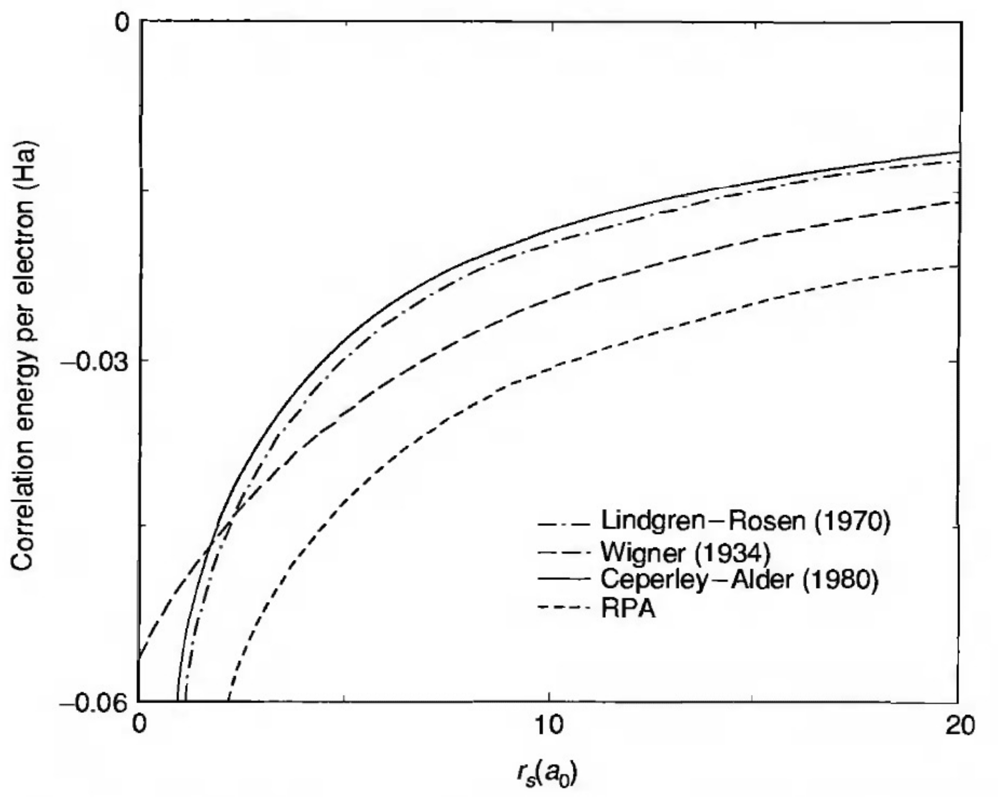

Figure 5.4. Correlation energy of an unpolarized homogeneous electron gas as a function of the density parameter r_s. The most accurate results available are quantum Monte Carlo calculations

From R. Martin “Electronic structure” book, p.109

Quantum Monte Carlo codes

QMCPACK

https://qmcpack.org

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CASINO

https://vallico.net/casinoqmc

RJ Needs, MD Towler, ND Drummond and P Lopez Rios
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